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NASA CONTRACTOR FINAL REPORT

CHEMICAL AND RHEOLOGICAL EVALUATION  
OF POLYIMIDES

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Space Administration

Langley Research Center  
Hampton, Virginia 23665

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## PREFACE

This document is the final report of the work accomplished under NASA Contract NAS1-16287, "A Study to Develop Reliable Manufacturing Cycles and In-Process Controls for High Temperature Resins for Graphite/Polyimide Composites" from August, 1980 through September, 1981.

The project was sponsored by Langley Research Center, National Aeronautics and Space Administration, Hampton, Virginia. Dr. T. St. Clair is Project Monitor.

The work was performed by the staff of Lockheed Missiles and Space Co., Inc., Advanced Manufacturing Technology, Organization 86-54. Dr. A. Wereta and Mr. M. Maximovich were principal technical investigators, while Mr. R. Galeos conducted the rheological studies. Other major contributors to the work included Mr. M Dusi, Ms. D. Hadad and Ms. C. Bostwick.

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## 1.0 INTRODUCTION

Graphite/polyimide composite materials exhibit high mechanical properties at elevated temperatures, low density, and excellent thermal-oxidative stability. They are, therefore, attractive candidates for many aerospace applications. However, the potential performance advantages will not be realized in production programs until reproducible, cost effective manufacturing procedures are established.

This work involves the chemical and rheological characterizations of several potential polyimide matrix resins to obtain the data required for reliable process development and control.

## 2.0 SUMMARY

The objective of the work was to develop chemical and rheological evaluation techniques for potential polyimide composite matrix materials that would lead to the development of improved, reliable manufacturing cycles and in-process controls. LARC 160 (AP-22), LARC 160 (Curithane 103), PMR 15, and PISO<sub>2</sub> resins were investigated during the course of the work. Liquid and solid state rheological testing proved efficacious in comparing and evaluating the resins and in developing preliminary processing parameters.

Significant similarities and differences were found among the addition cure type polyimide matrix resins. Woven graphite cloth reinforced laminates were successfully fabricated, using parameters obtained from the rheological data generated during the course of the work.

## 3.0 CHEMICAL CHARACTERIZATION

### 3.1 Synthesis of LARC 160 Resins

Samples of LARC 160 (AP-22) and LARC 160 (Curithane 103) were synthesized according to the appropriate procedures outlined in the appendix. After checking with Dr. St. Clair, a one-to-one substitution of Curithane 103 for Jeffamine AP-22 was made. Curithane 103 was considerably more difficult to soften or dissolve than Jeffamine AP-22. This behavior seems consistent with the isomer concentrations listed in Table 3-1. Curithane 103 has the highest concentration of 4,4' MDA and as such it is expected to have a more crystalline nature. The PMR 15 polyimide reported herein was synthesized using ethanol rather than methanol.



In order to verify chemical structures, IR spectroscopy and liquid chromatography were employed. Samples of both LARC 160 batches appear to show no significant differences in IR absorption peaks.

As synthesized, the volatile content of each LARC 160 batch was running about 48%. This was determined by inserting a resin sample into a preheated oven at 316°C for 30 minutes and then calculating the sample weight loss. This figure includes both solvent and condensation by-products. In order to be more representative of resin found in a prepreg, it was decided that a realistic volatile to resin ratio should be determined and also that the as-synthesized resin should be dried to this level. The dry resin content (after 30 minutes at 316°C) and volatile content (same conditions) of fabric LARC 160 prepreg used at LMSC runs around 36% and 12%, respectively. This gives a ratio of 1:3 or in other words 25% of the net resin weight is volatile. Drying conditions of 50°C for 2 to 3 hours in a vacuum oven seem to be appropriate and IR data shows no side reaction products.

### 3.2 HPLC Evaluation

An HPLC procedure for the quality assurance of the synthesized polyimide resins was evaluated. The test procedure used is outlined in Reference 1. In our case the aqueous portion of the gradient mobile phase was not buffered with  $\text{KH}_2\text{PO}_4$ . However, the change did not appear to affect the quality of the component separations.

#### Liquid Chromatography Test Conditions:

$\mu$  BONDAPAK C<sub>18</sub> Column (Waters Assoc.)

U.V. @ 200nm, 0.5AUFS, Band Width 16nm, Time Constant @ Normal (Varian VARICHROM)

U.V. @ 254nm, 0.2AUFS (Waters Assoc. 440 Detector)

10% → 50%  $\text{CH}_3\text{CN}$  (Waters Assoc.) vs.  $\text{H}_2\text{O}$  (J. T. Baker)

15 min. Linear Gradient, 10 min. Hold @ Final, 15 min. Equilibration Delay

Flow Rate @ 1.0 ml/min

The necessity of the buffer to obtain "good" separations seems to depend on the sum total effects of all test parameters as well as the desired end use of the resultant chromatogram. The use of a buffer in polyimide analysis appears not to be universal with all investigators so the decision was made to first analyze the synthesized resins with pure solvents.

TABLE 3-1 RESULTS OF QUANTITATIVE ANALYSIS ON  
POLYAMINE MIXTURES (REF. 2)

PERCENT METHYLENEDIANILINE				
SAMPLE	2,2'-(1)	2,4'	4,4'-	$\Sigma$
AP-22	14.18	20.97	48.73	83.88
Tonox	4.24	14.80	61.21	80.25
Curithane-103	1.62	2.78	73.89	78.29
Anacamine DL	5.63	23.36	42.35	71.34
Tonox LC <sup>(2)</sup>	8.01	11.15	51.27	70.43
Tonox 22	0.78	3.98	54.75	59.51
Tonox JB	2.67	9.80	36.97	49.44
Tonox 60/40	1.60	8.71	37.85	48.16
Poly MDA	---	---	4.36 <sup>(3)</sup>	4.36
2,4-Bis(p-amino- benzyl)aniline	---	---	1.83 <sup>(3)</sup>	1.83

Footnotes: (1) 2,2'-MDA peak may be integrated with 4,4'-diamino-3-methyldiphenylmethane peak.  
(2) Peaks for 2,2'-MDA and 2,4'-MDA were not well resolved.  
(3) Value is questionable due to long retention time.

The chromatograms at 254 nm of the gradient blank, the starting materials, the half ester samples and each synthesized resin are shown in Figures 3-1 through 3-12. For comparison of the responses at 200 nm the chromatograms for the blank and neat resins are shown in Figures 3-13 through 3-16. No attempt was made to optimize integration so the % Peak Area results are not included since integration points were not consistent. The differences between the responses at 200 nm and 254 are not substantial. Note that using these test conditions nadic anhydride is not detected.

To determine the effects of staging on the separated peaks, resins staged in the Rheometrics were analyzed by HPLC. The chromatogram comparison is shown in Figure 3-17. Keep in mind that the resin staged 1 hour at 121°C was not completely soluble in acetonitrile. Thus, the curve represents resin that was soluble and prefiltered through a 0.45  $\mu$  fluoromembrane filter. As can be seen, there are obvious effects on all peaks as the result of staging. Slight changes are evident even for the resin drying period of 2 hours at 50°C. The significance of these differences is not known at this time. Radical variations are seen in the extreme case of 1 hour staging at 121°C. The main reaction peak predominates in this curve.

General identification of specific peaks is made in a few instances. Lack of chromatogram complexity as compared to that obtained by Rockwell may be attributed to two factors. First, our syntheses were carried out in fairly pure ethanol whereas Rockwell's esterification was conducted using an industrial alcohol mixture. Second, our resins were prepared under dilute solvent conditions. According to the 9th Quarterly Report (June - September, 1980) from Rockwell (Ref. 3), high viscosity during the co-esterification of the starting anhydride materials results in incomplete conversion of BTDA to the BTDE diester and, thus, the presence of the BTDA tetra-acid (BTA) and BTDE monoester will be evident.

The infrared spectra of the three synthesized resins are shown in Figures 3-18 to 3-20. Comparing these with our previous work and that done on the CASTS Program, there is some confusion as to the significance of the doublet at 1050  $\text{CM}^{-1}$ . In most references this region always displays a singlet around 1060  $\text{CM}^{-1}$  and has been associated with the ethyl ester intermediate of BTDA.

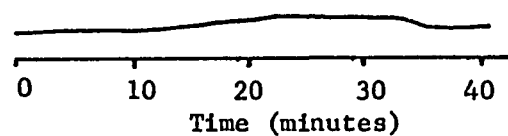
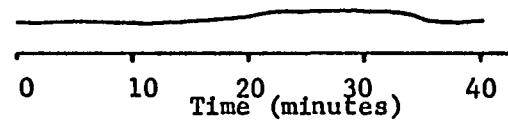
5  $\mu$ lFigure 3-1 BLANK (CN<sub>3</sub>CN)5  $\mu$ l of 0.86  $\mu$ g/ $\mu$ l CH<sub>3</sub>CN

Figure 3-2 Chromatogram of Nadic Anhydride

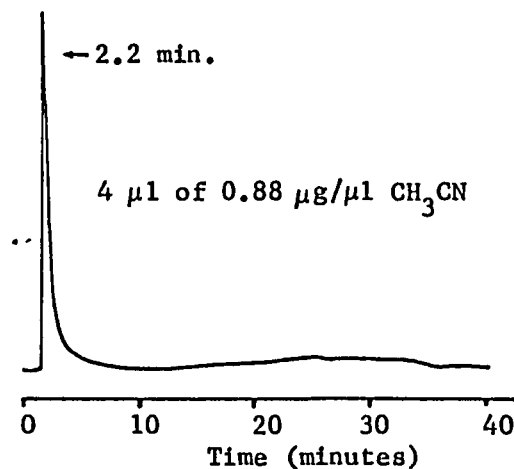


Figure 3-3 Chromatogram of 3,3', 4,4'-BTDA

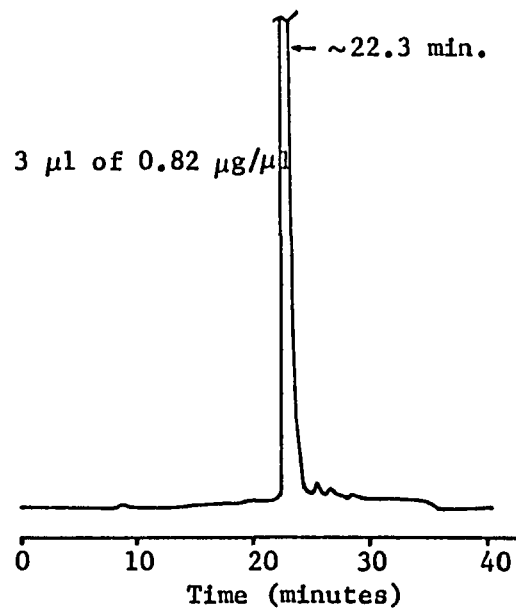


Figure 3-4 Chromatogram of 4,4'-MDA

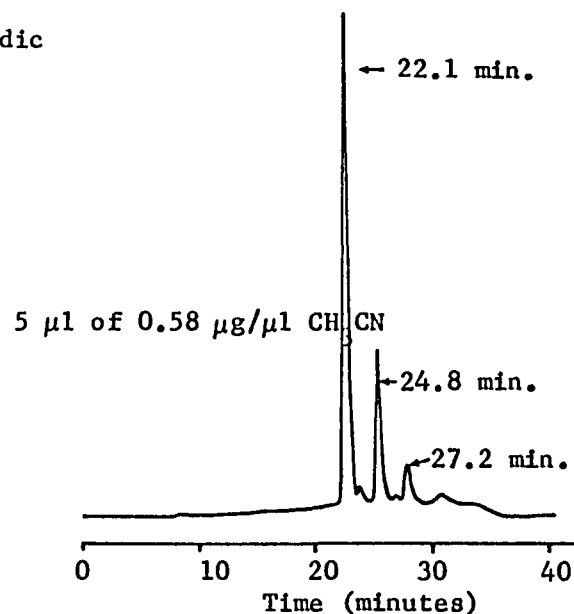


Figure 3-5 Chromatogram of Jeffamine AP-22

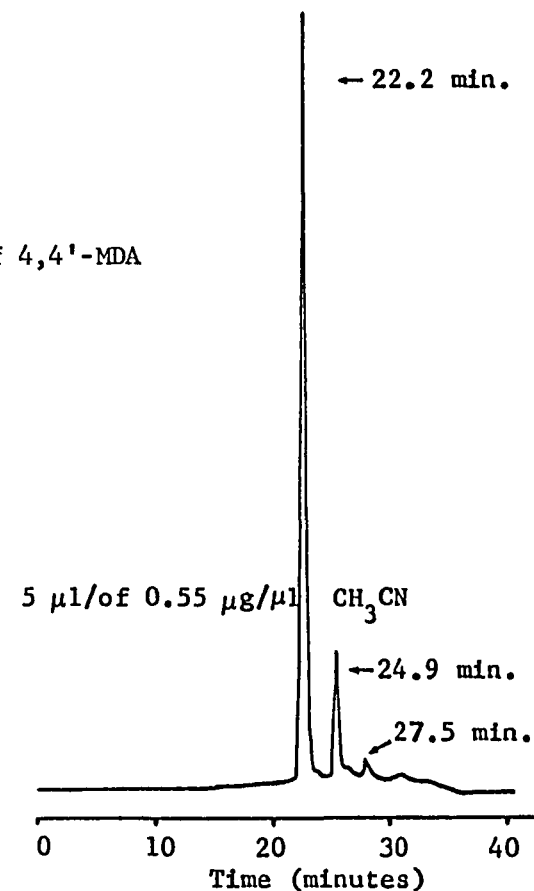


Figure 3-6 Chromatogram of Curithane 103

254 nm

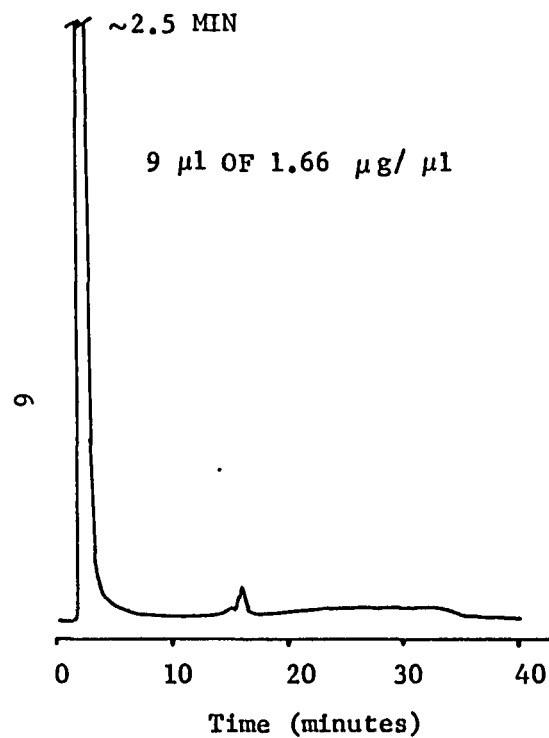


Figure 3-7

Chromatogram of 1/2 Ester of LARC 160  
W/AP-22

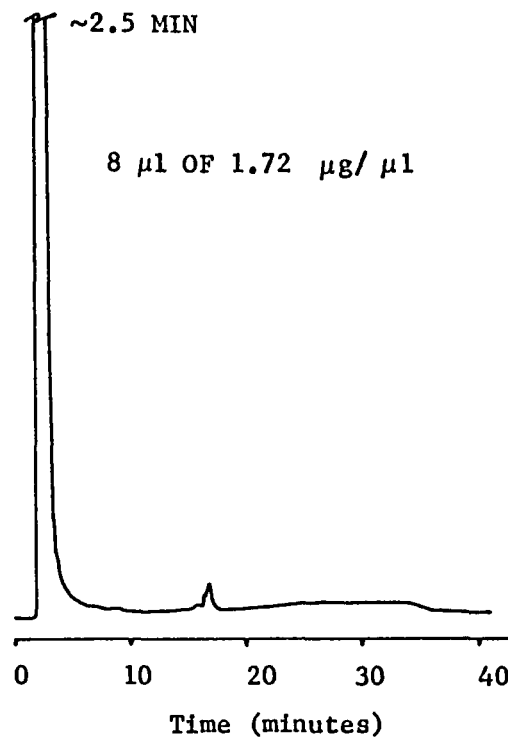


Figure 3-8

Chromatogram of 1/2 Ester of LARC 160  
W/Curithane 103

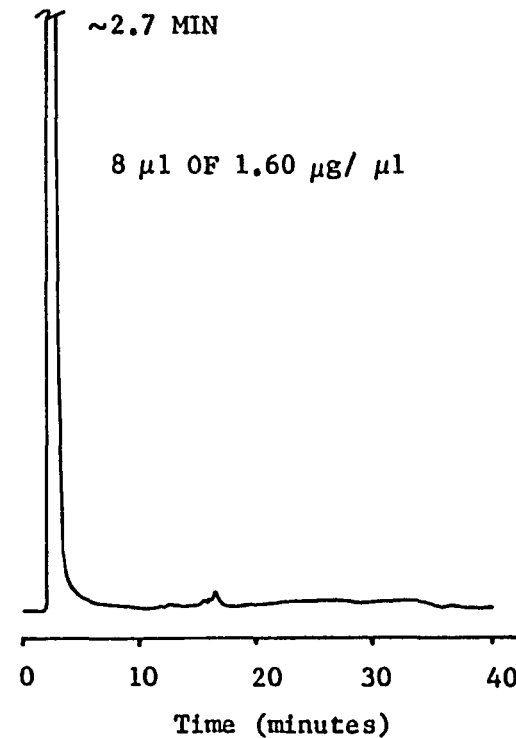


Figure 3-9

Chromatogram of 1/2 Ester of  
PMR-15

254 nm

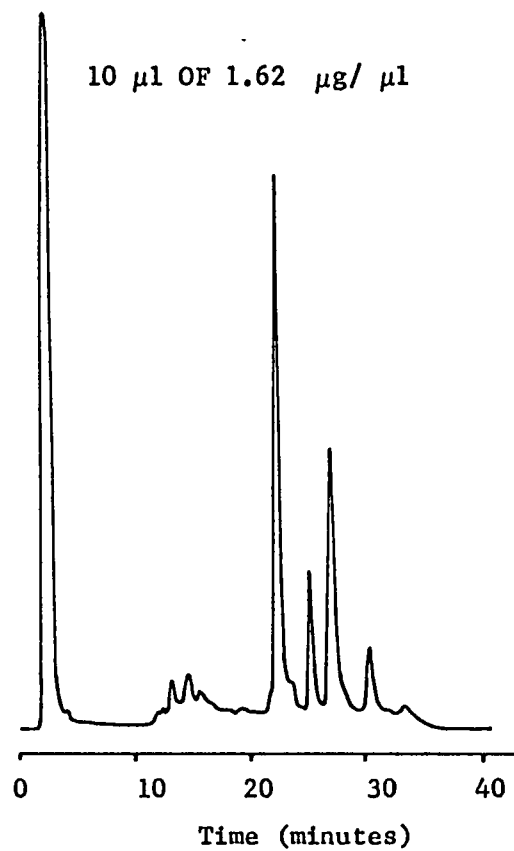


Figure 3-10  
Chromatogram of LARC 160 W/AP-22

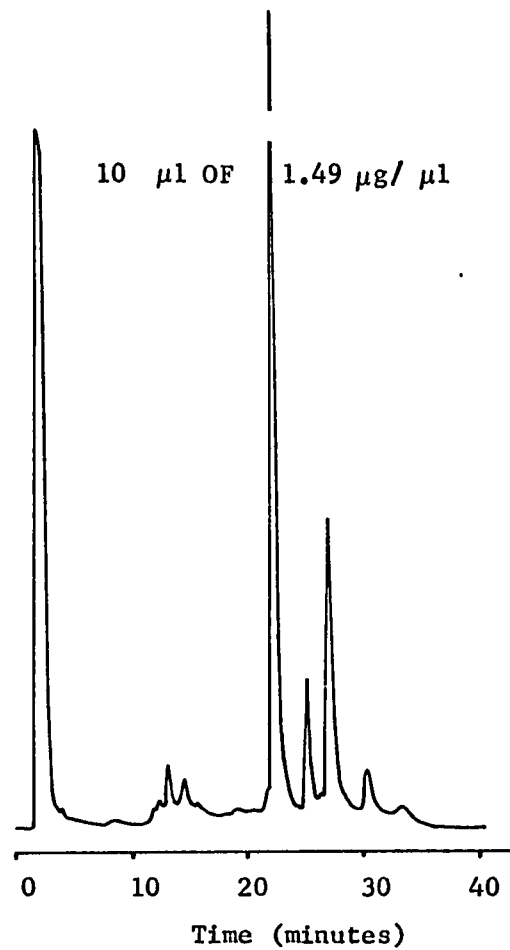


Figure 3-11  
Chromatogram of LARC 160 W/Curithane 103

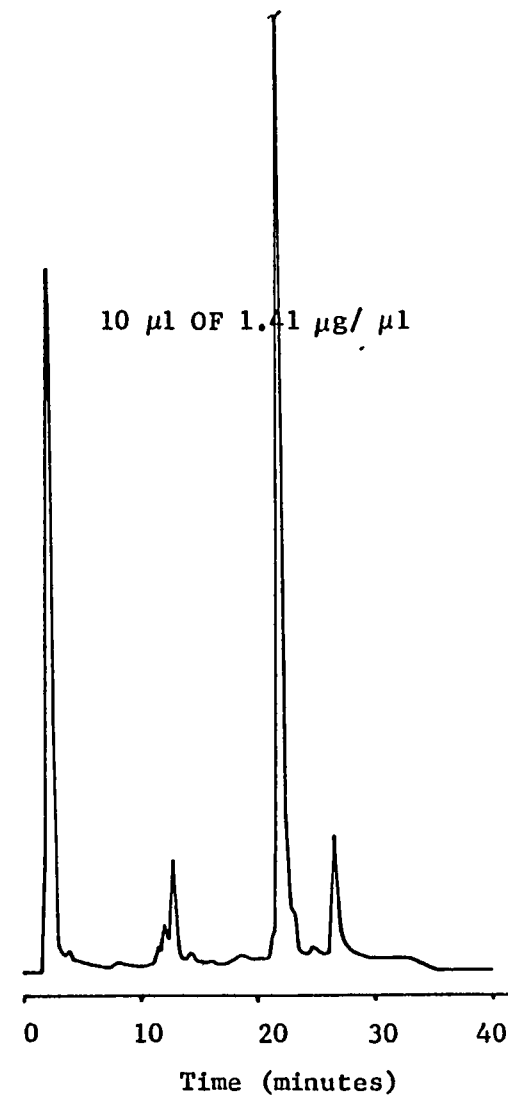
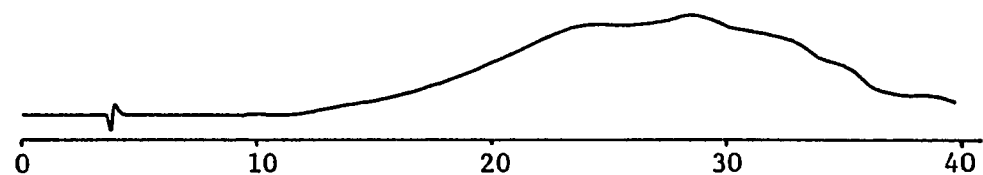


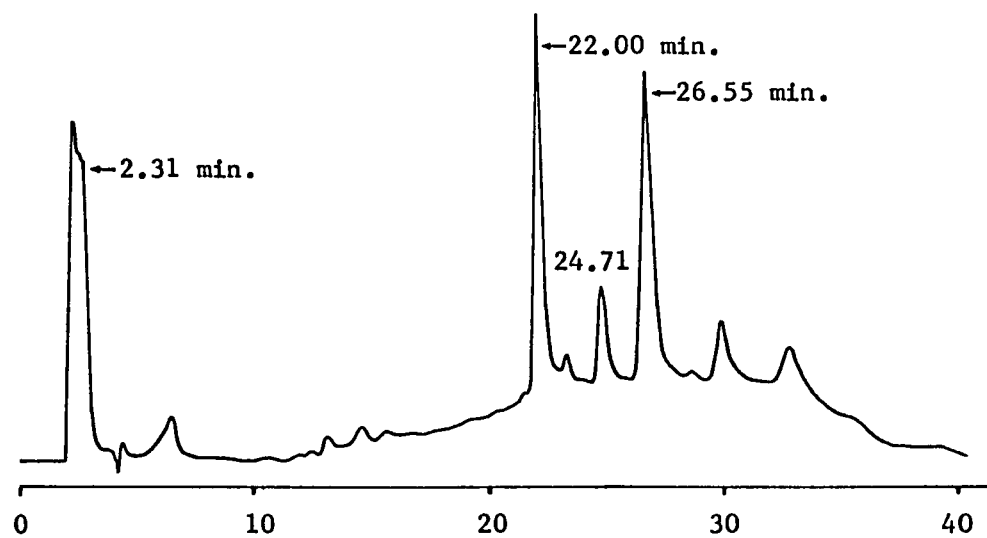
Figure 3-12  
Chromatogram of PMR-15

200 nm



Time (minutes)

Figure 3-13 Chromatogram of Blank (CH<sub>3</sub>CN)



Time (minutes)

Figure 3-14 Chromatogram of LARC 160 with AP-22

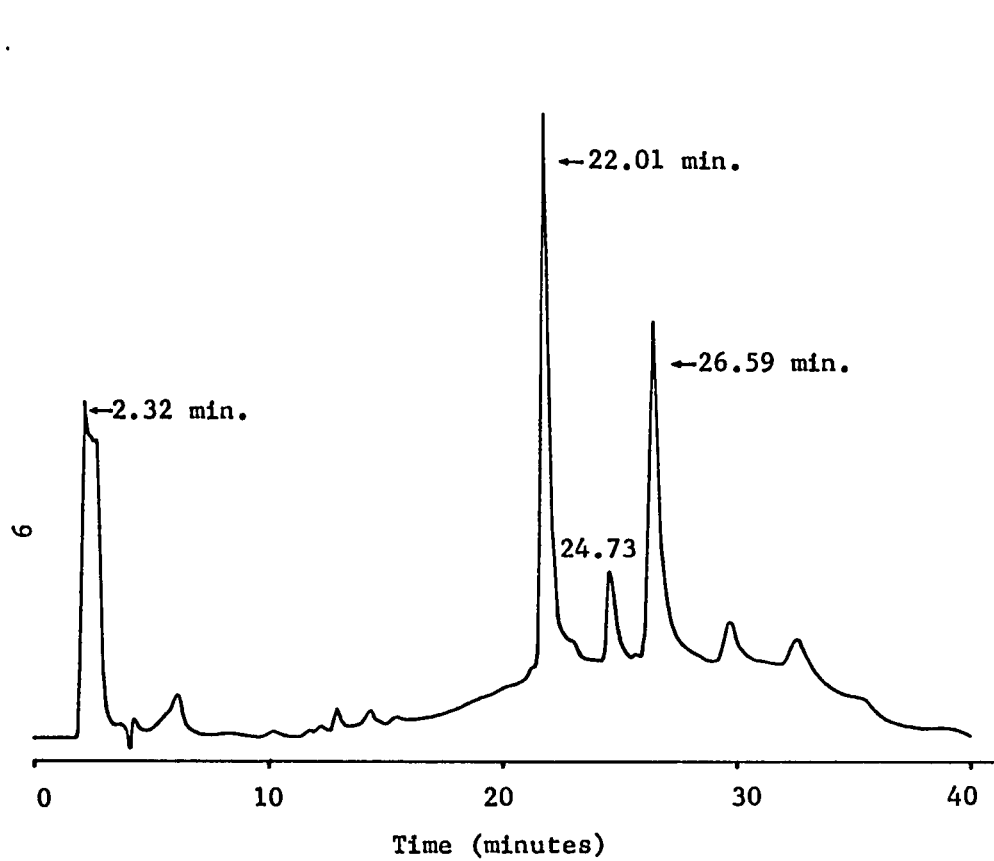


Figure 3-15

Chromatogram of LARC 160 with Curithane 103

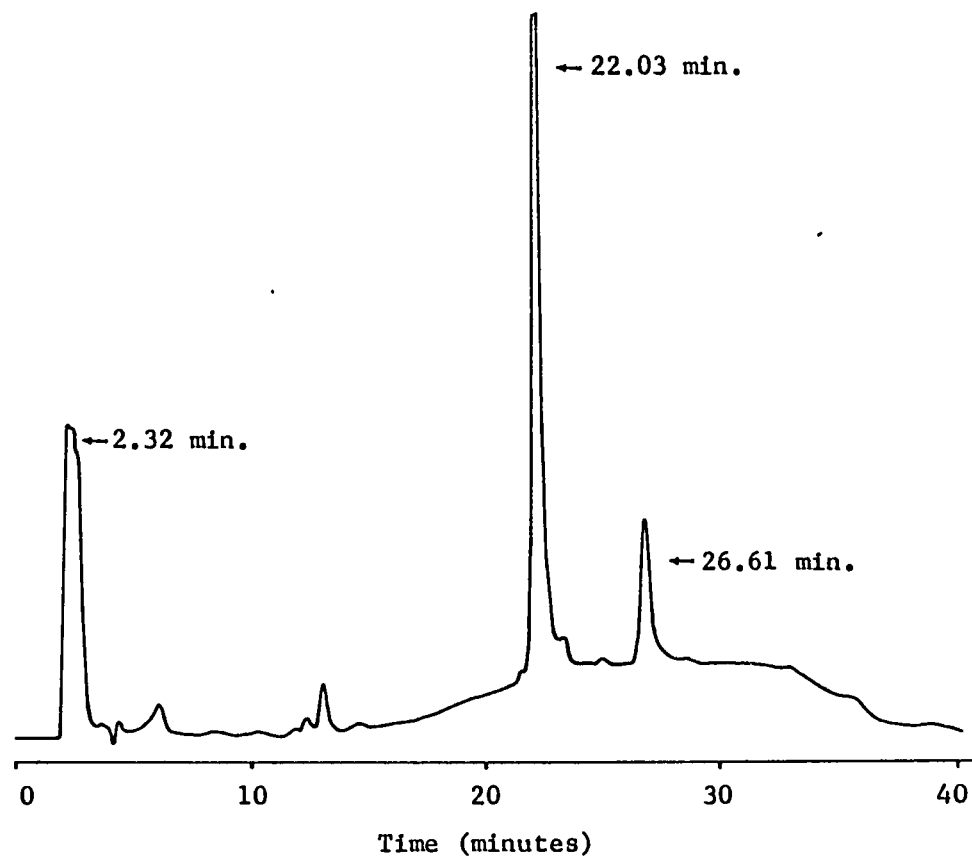


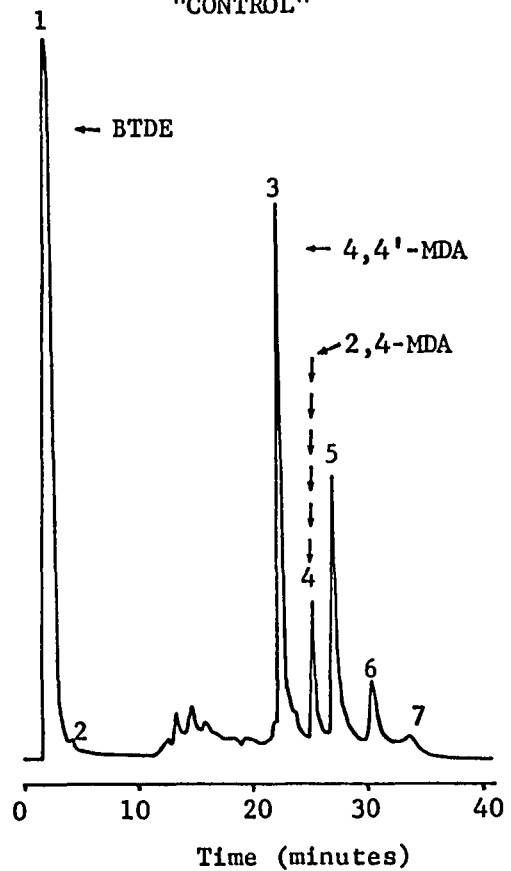
Figure 3-16

Chromatogram of PMR-15

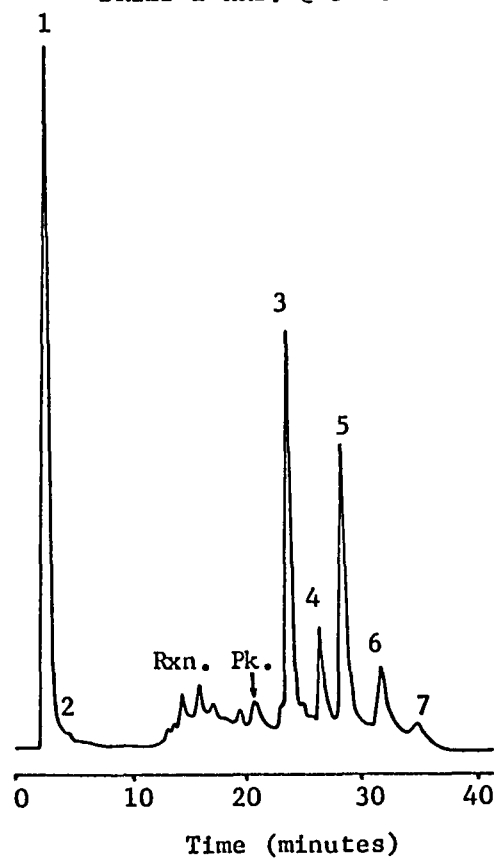


254 nm  
0.2 AUFS

LARC 160 WITH AP-22  
"CONTROL"



DRIED 2 HRS. @ 50°C



STAGED 1 HR. @ 121°C

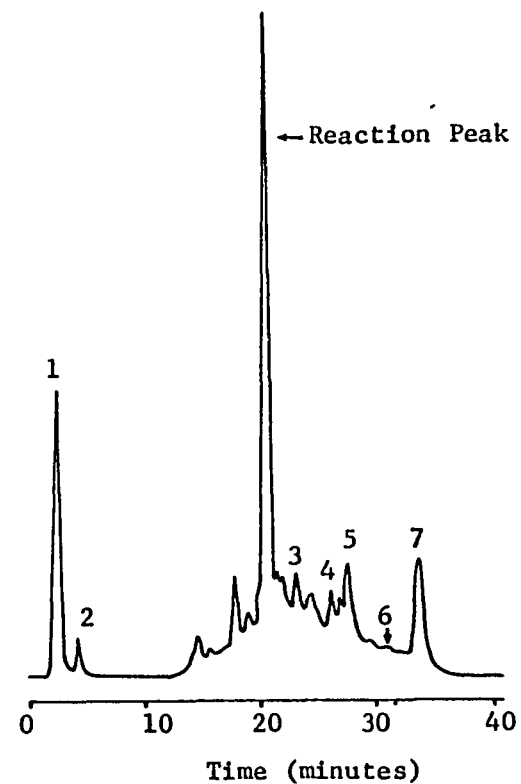


Figure 3-17 Effects of Staging on HPLC Chromatograms

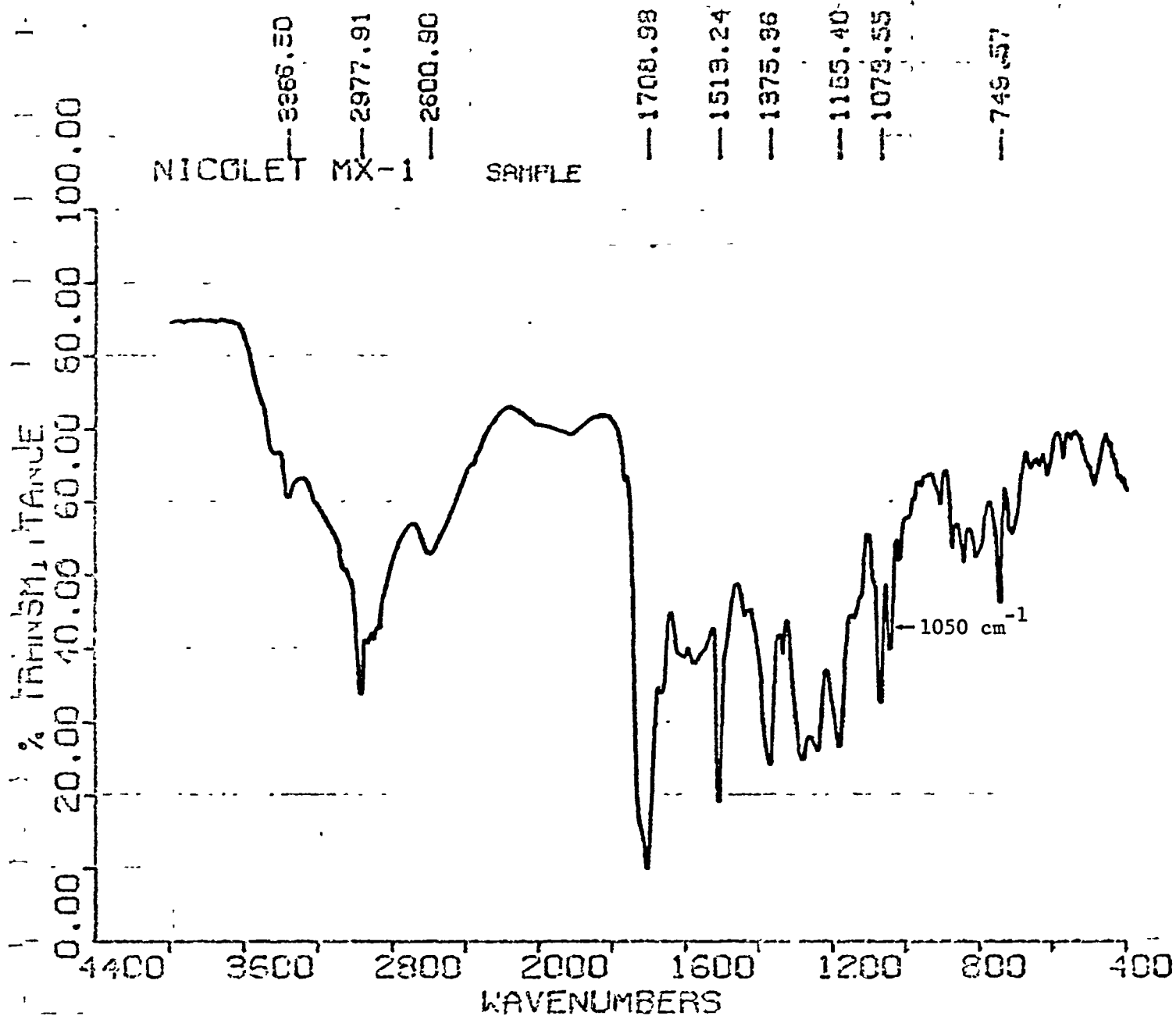


Figure 3-18  
IR of Synthesized LARC 160 with Jeffamine AP-22

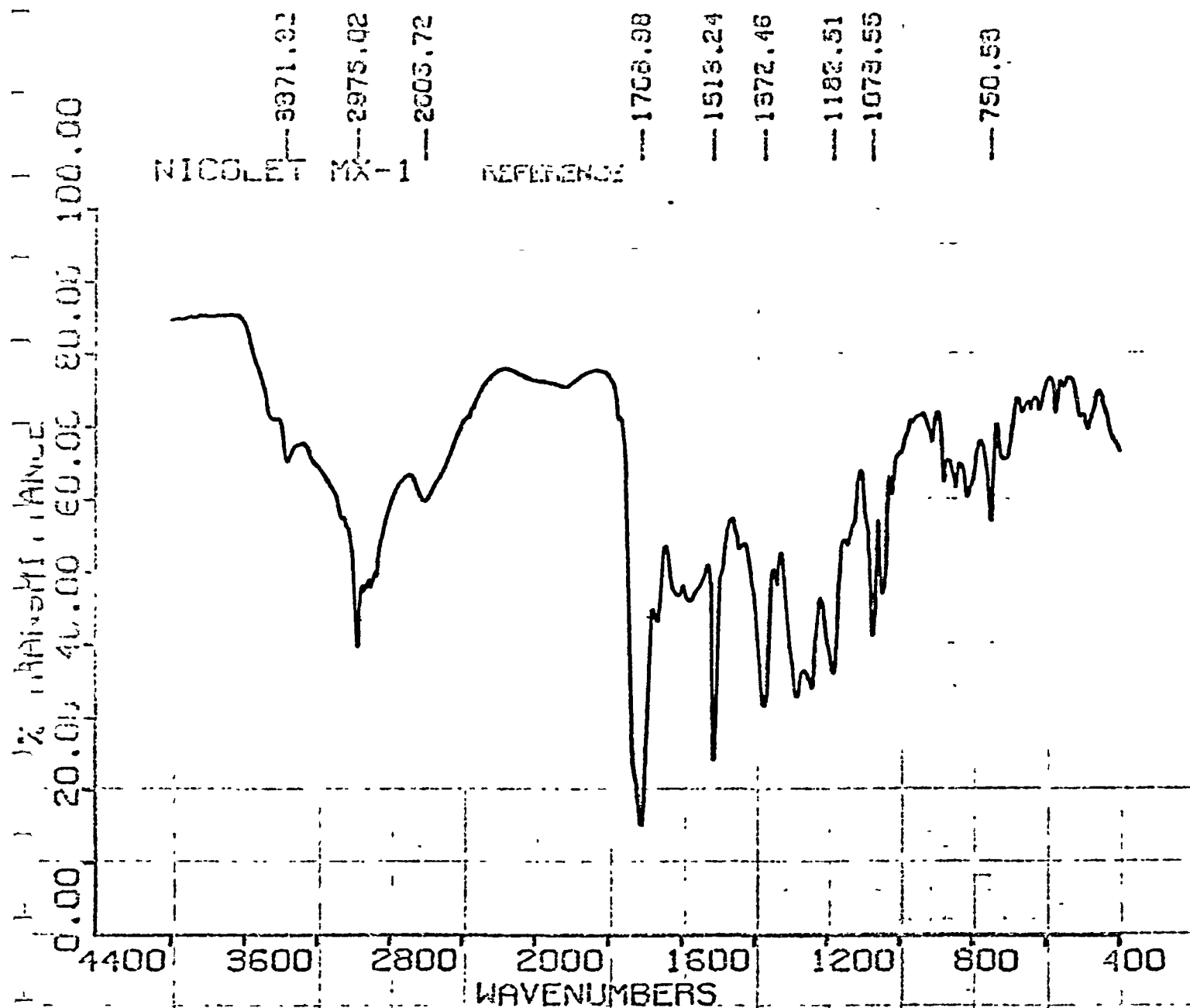


Figure 3-19

IR of Synthesized LARC 160 with Carithane 103

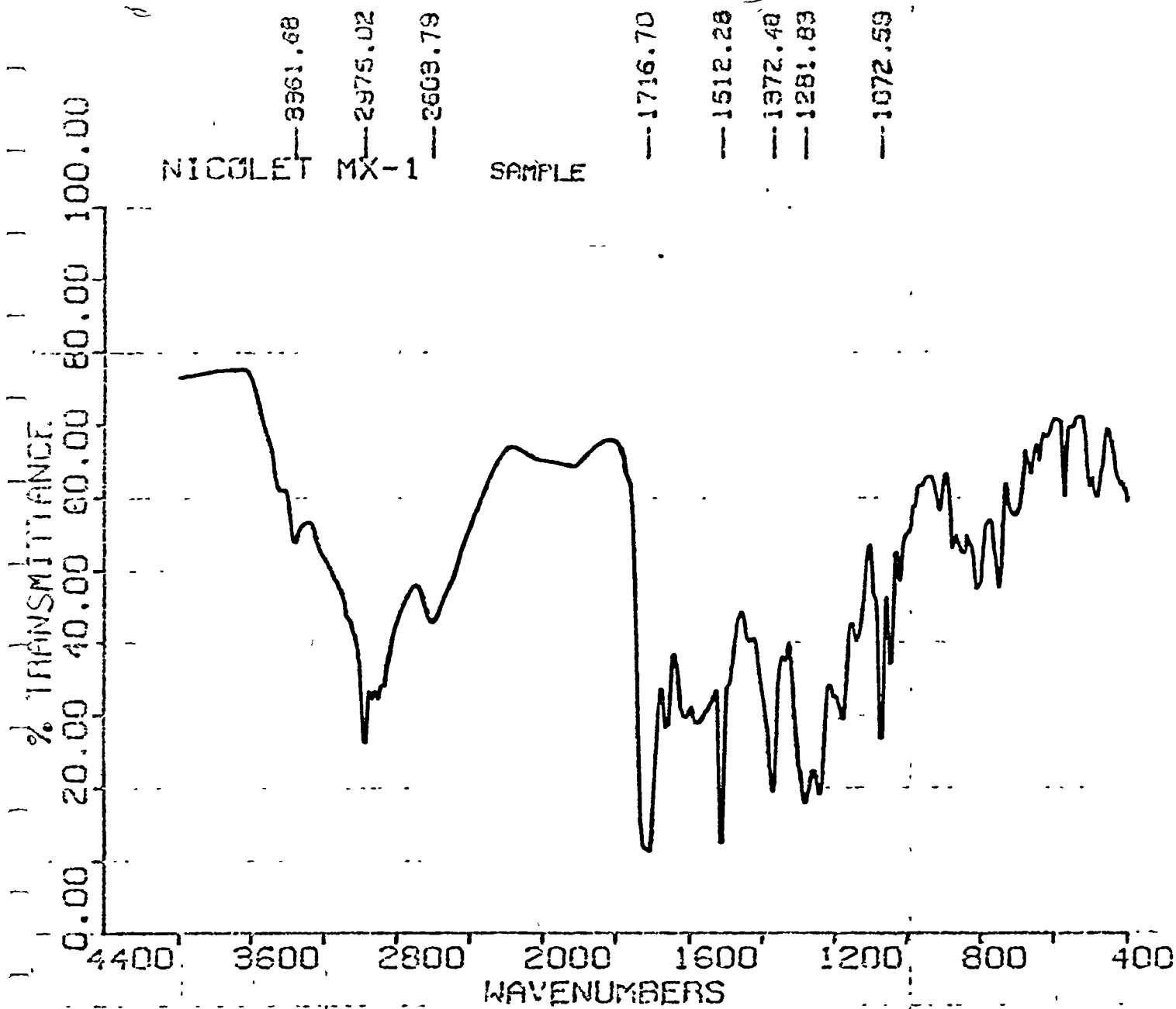


Figure 3-20  
IR of Synthesized PMR-15

In Rockwell's 2nd Quarterly Report (NAS1-15371) Ref. 4, a doublet is present in spectra of the ethyl ester of nadic anhydride. Rockwell's curves are shown in Figures 3-21 and 3-22 for comparison.

### 3.3 Characterization of 500 Gram Batches

Two additional 500g batches of both AP-22 and Curithane 103 based LARC 160 were next synthesized according to the procedure in the appendix. A similar size batch of PMR-15 was also prepared, using methanol solvent this time.

DSC studies were carried out on both unstaged resin and resin staged 1/2 hour at 120°C. Only minor differences were noted between the two LARC 160 versions. A set of curves was also run on the PMR-15 batch and is included for comparative purposes. Figure 3-23 through 3-28 show this data. Figures 3-29 through 3-34 show the same data for the earlier LARC 160 and PMR-15 batch.

### 3.4 Preparation of Neat Resin Moldings

In order to run TMA (as well as solid state rheological studies) on the two LARC 160 resins, it was necessary to prepare neat resin moldings. This was not an insignificant task, as a staging cycle was required that allowed the powdered resin to be cured under pressure. Simple casting and curing or pressing to stops resulted in high void moldings or moldings with incomplete consolidation. After talks with the NASA Technical Representative, we developed cycles for both resin systems. The Curithane based LARC 160, however, required significantly more staging than the AP-22 version to achieve the low flow characteristics required to produce satisfactory moldings. The staging cycles\*, shown in Table 3-2 were used:

Table 3-2 LARC 160 Staging for Molding Compounds

	<u>AP-22 LARC 160 Cycle</u>	<u>Curithane LARC 160 Cycle</u>
Step:	1. 140°C - 90 min.	1. 140°C - 90 min.
	2. 140°C - 30 min.	2. 140°C - 30 min.
	3. 180°C - 60 min.	3. 180°C - 60 min.
	4. 210°C - 30 min.	4. 210°C - 60 min.
	<u>5. 250°C - 60 min.</u>	5. 220°C - 60 min.
	4.5 Hours Total	<u>6. 250°C - 75 min.</u>
		6.25 Hours Total

\*Resin was ground between staging steps to facilitate volatile removal.

Infrared Spectra from Rockwell International

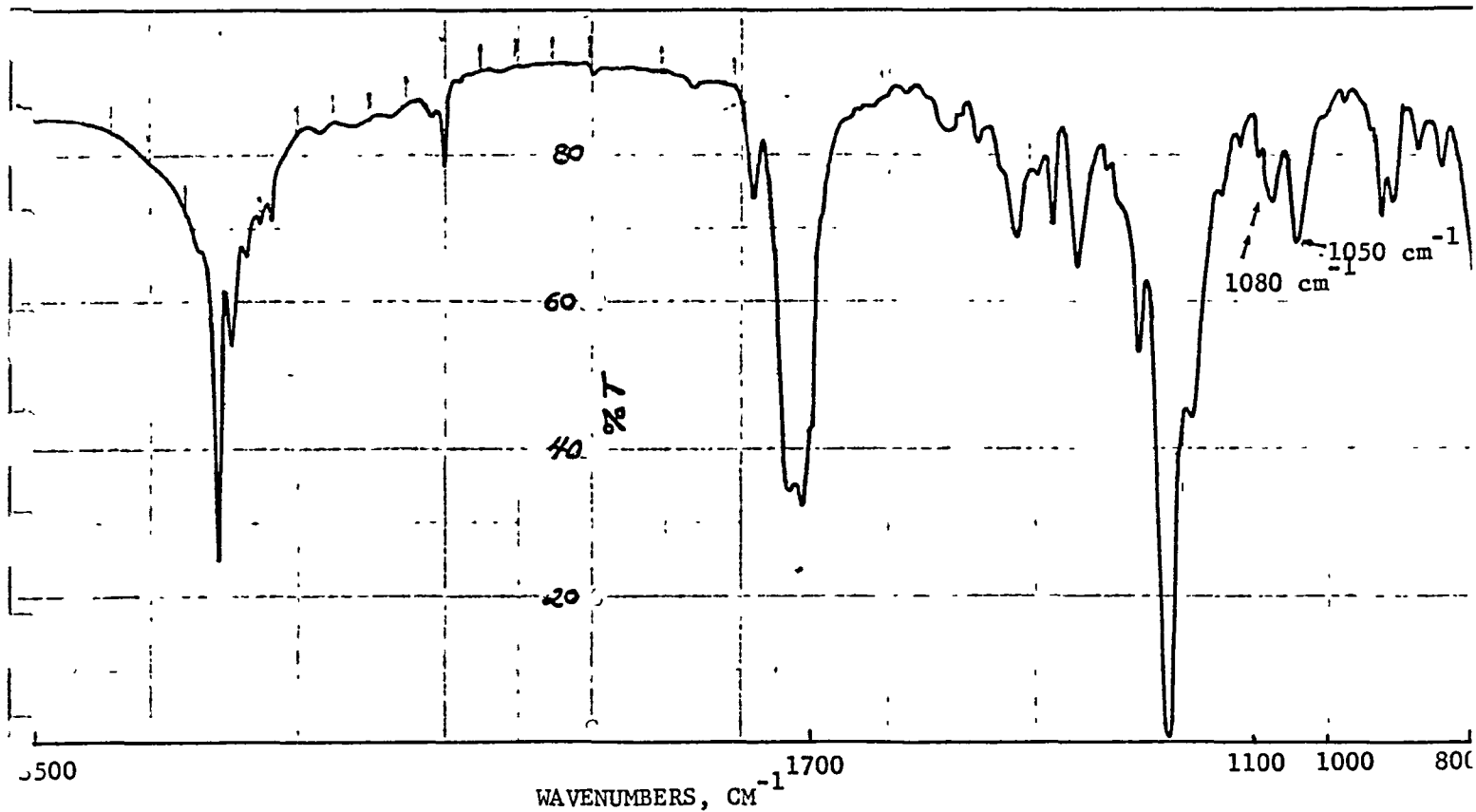


Figure 3-21 IR Spectrum of Monoethyl ester of NA

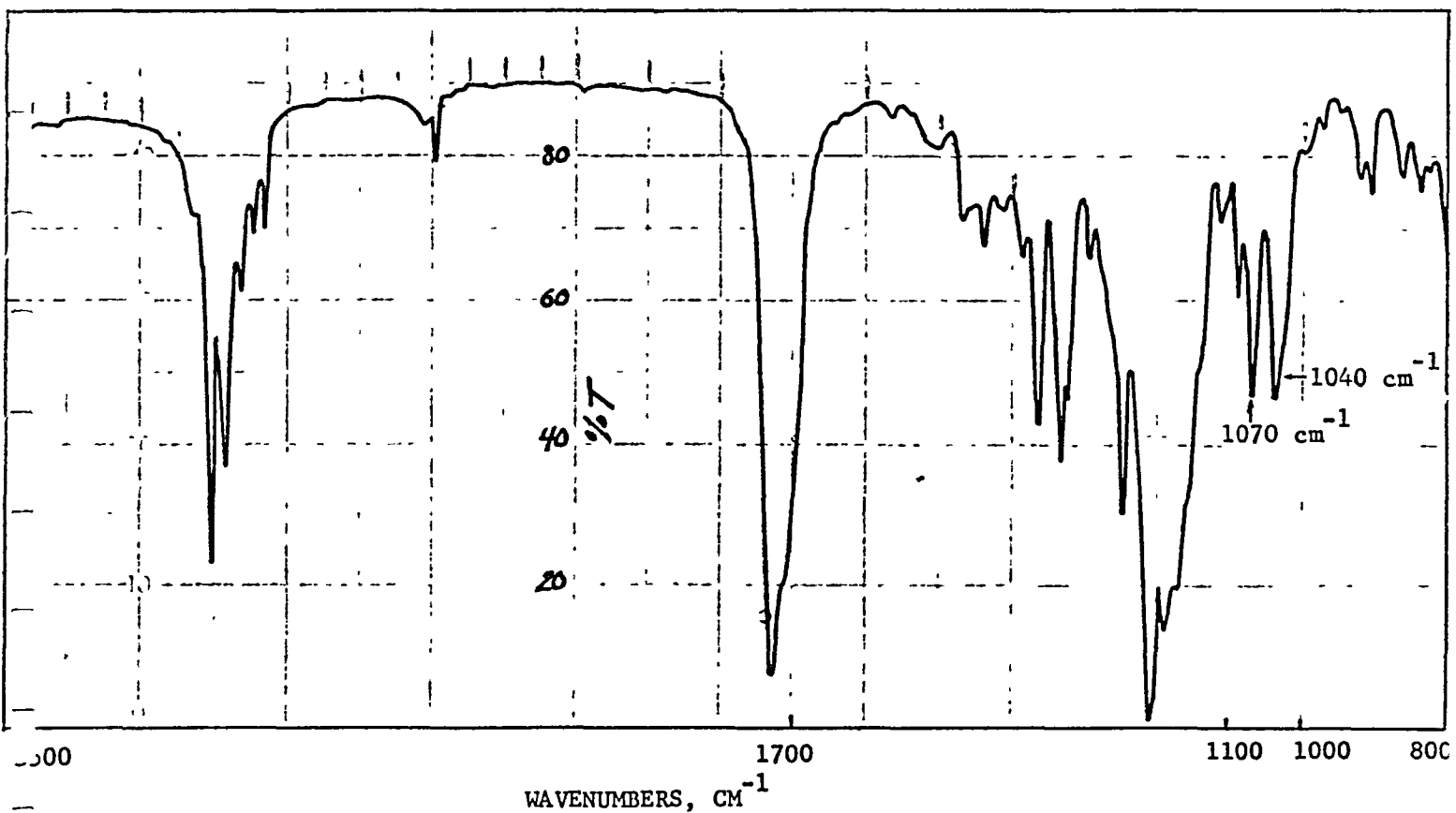


Figure 3-22 IR Spectrum of Diethyl Ether of NA

FIG. 3-23  
DSC OF LARC 160/103 UNSTAGED

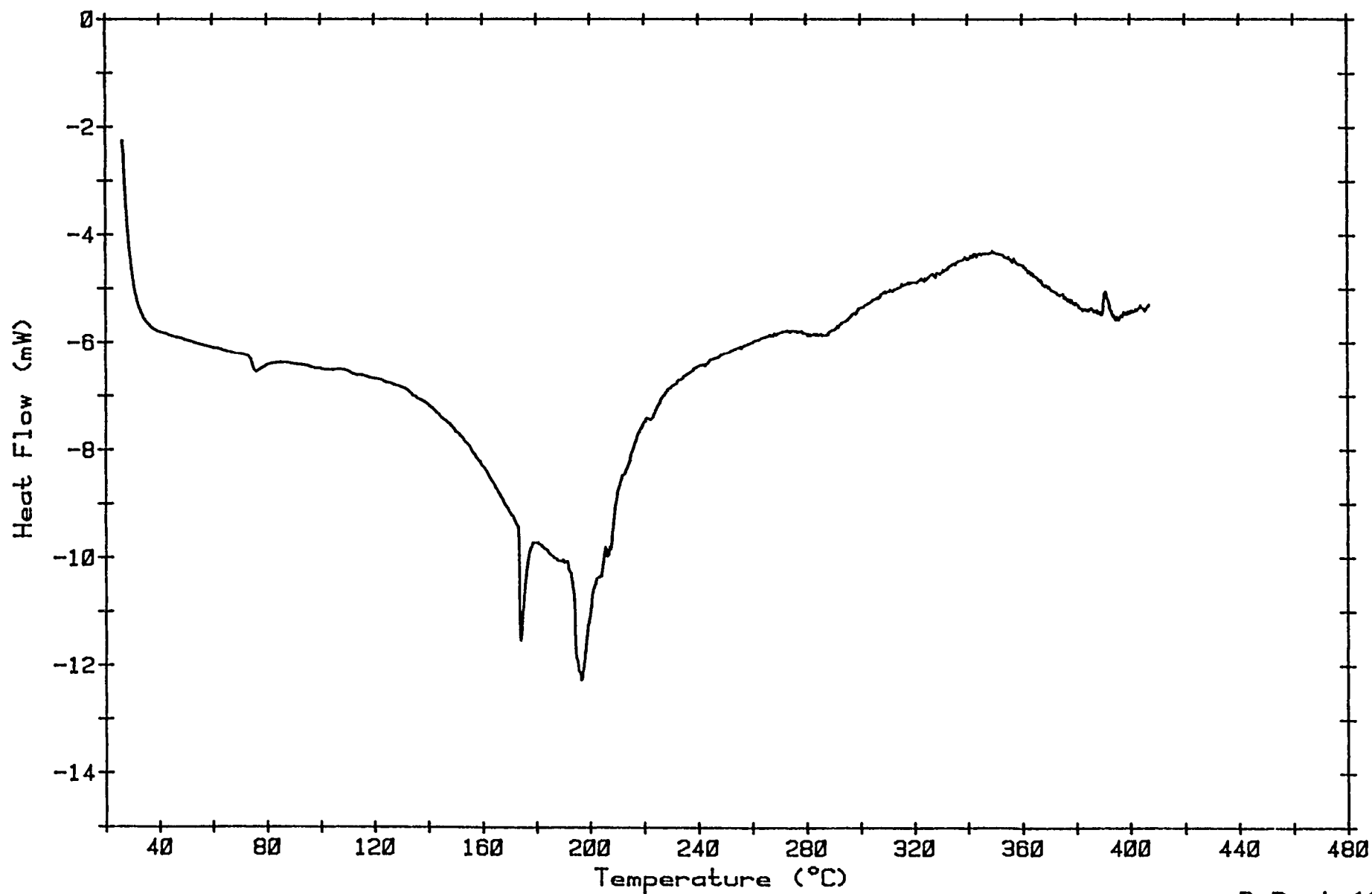


FIG. 3-24  
DSC OF LARC 160/103 STAGED .5 HR/120 C.

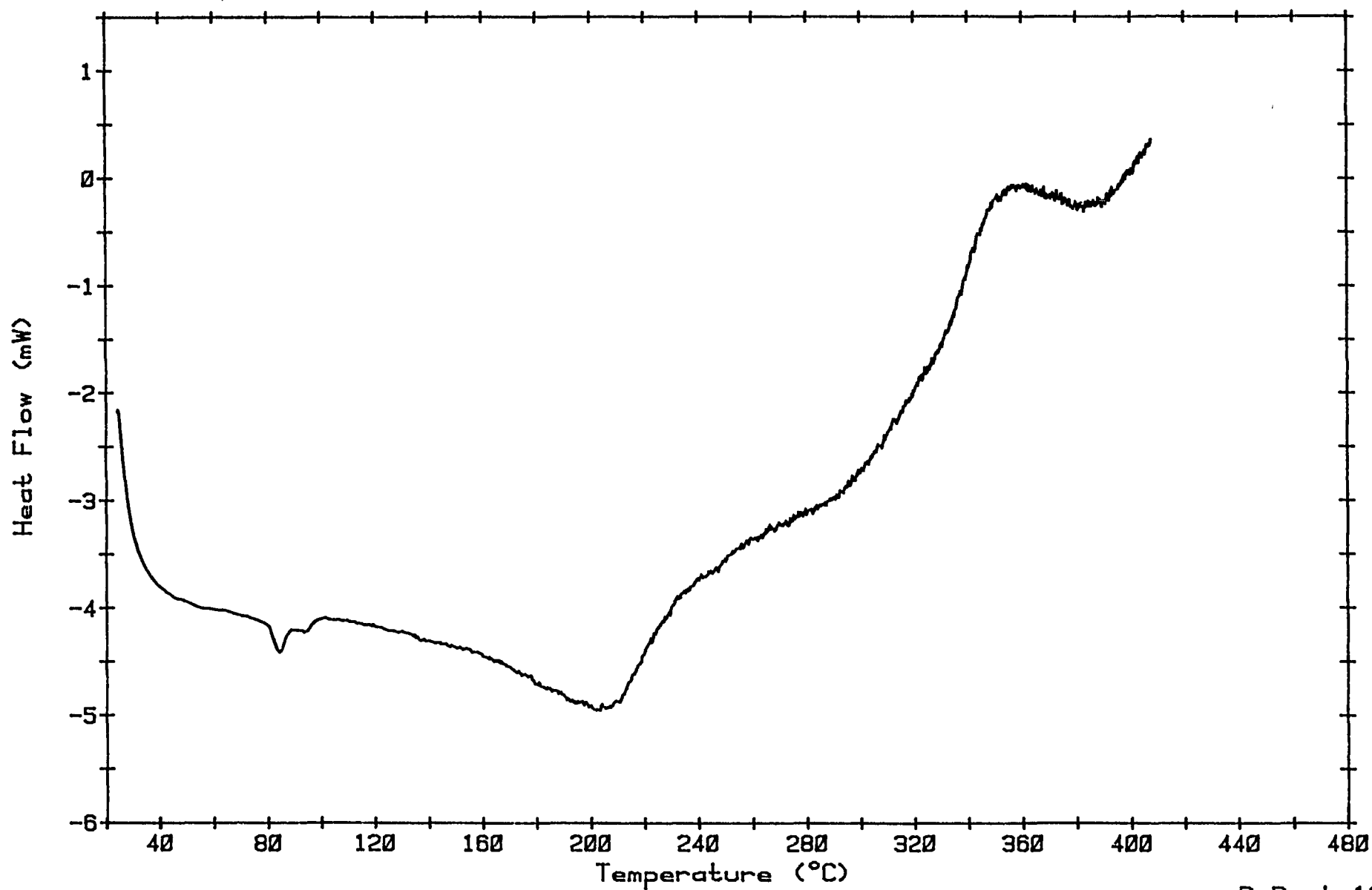




FIG. 3-25  
DSC OF LARC 160/22 UNSTAGED

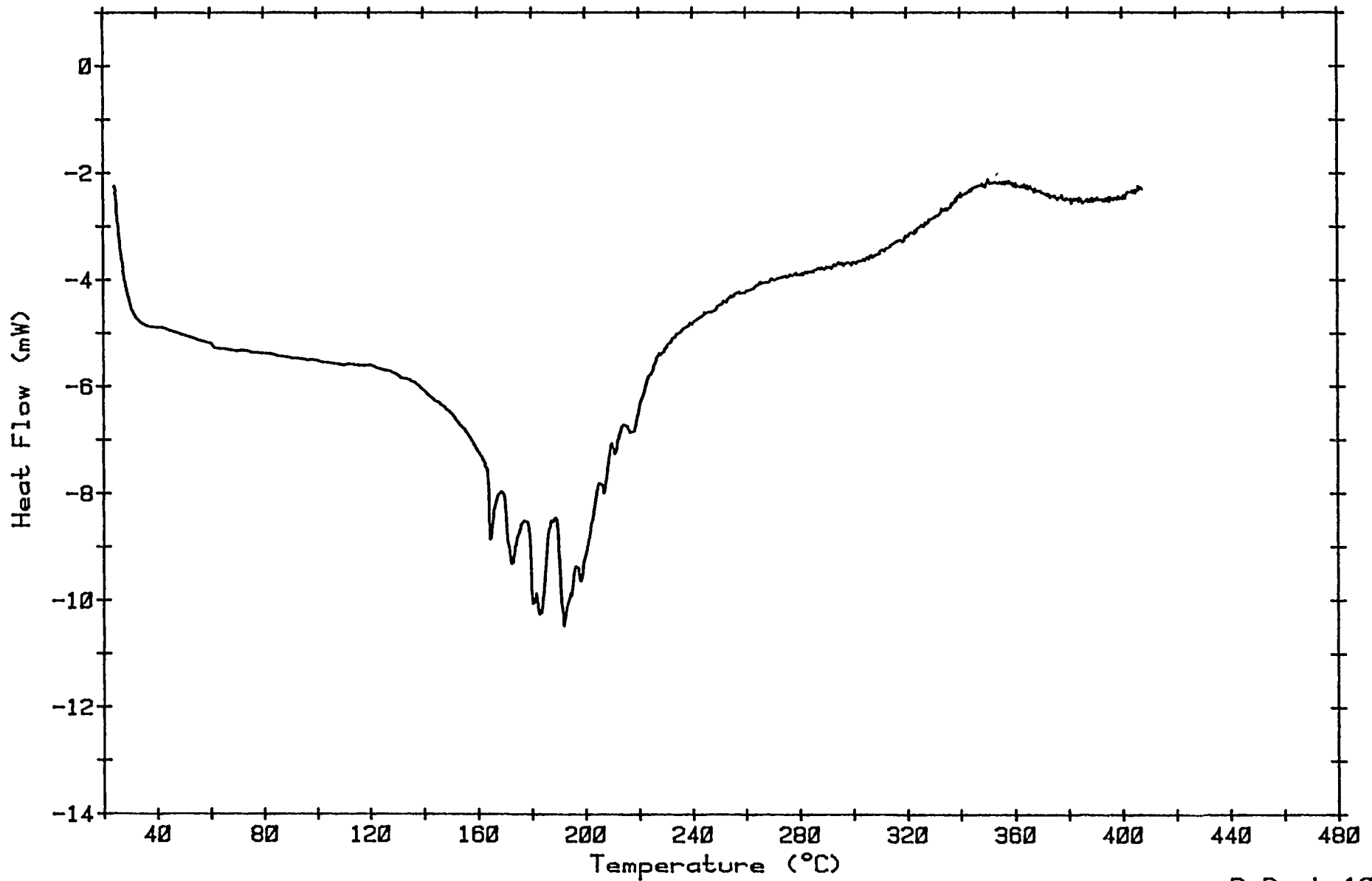


FIG. 3-26  
DSC OF LARC 160/22 STAGED .5 HR/120 C

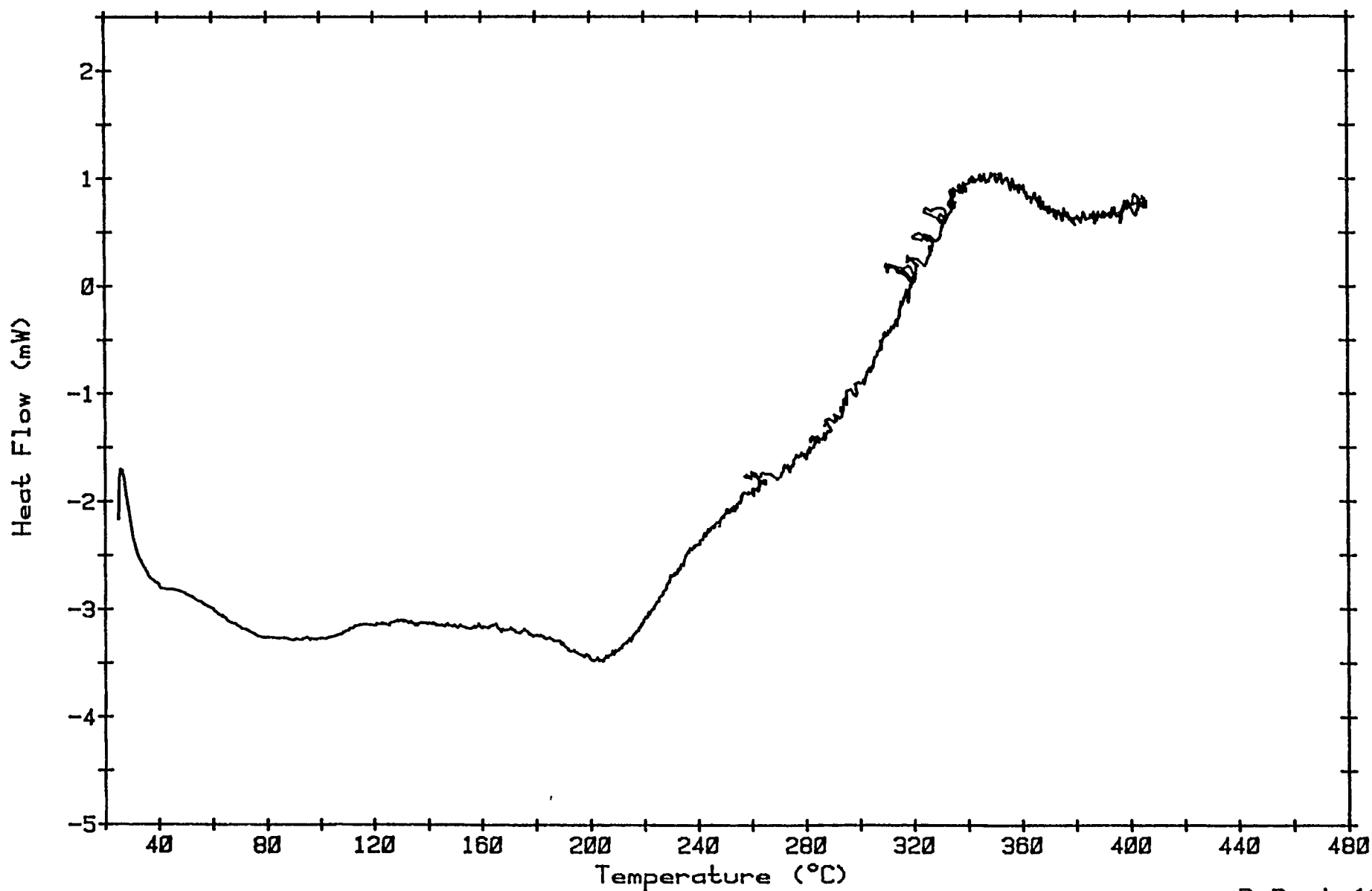


FIG. 3-27  
DSC OF PMR-15 UNSTAGED

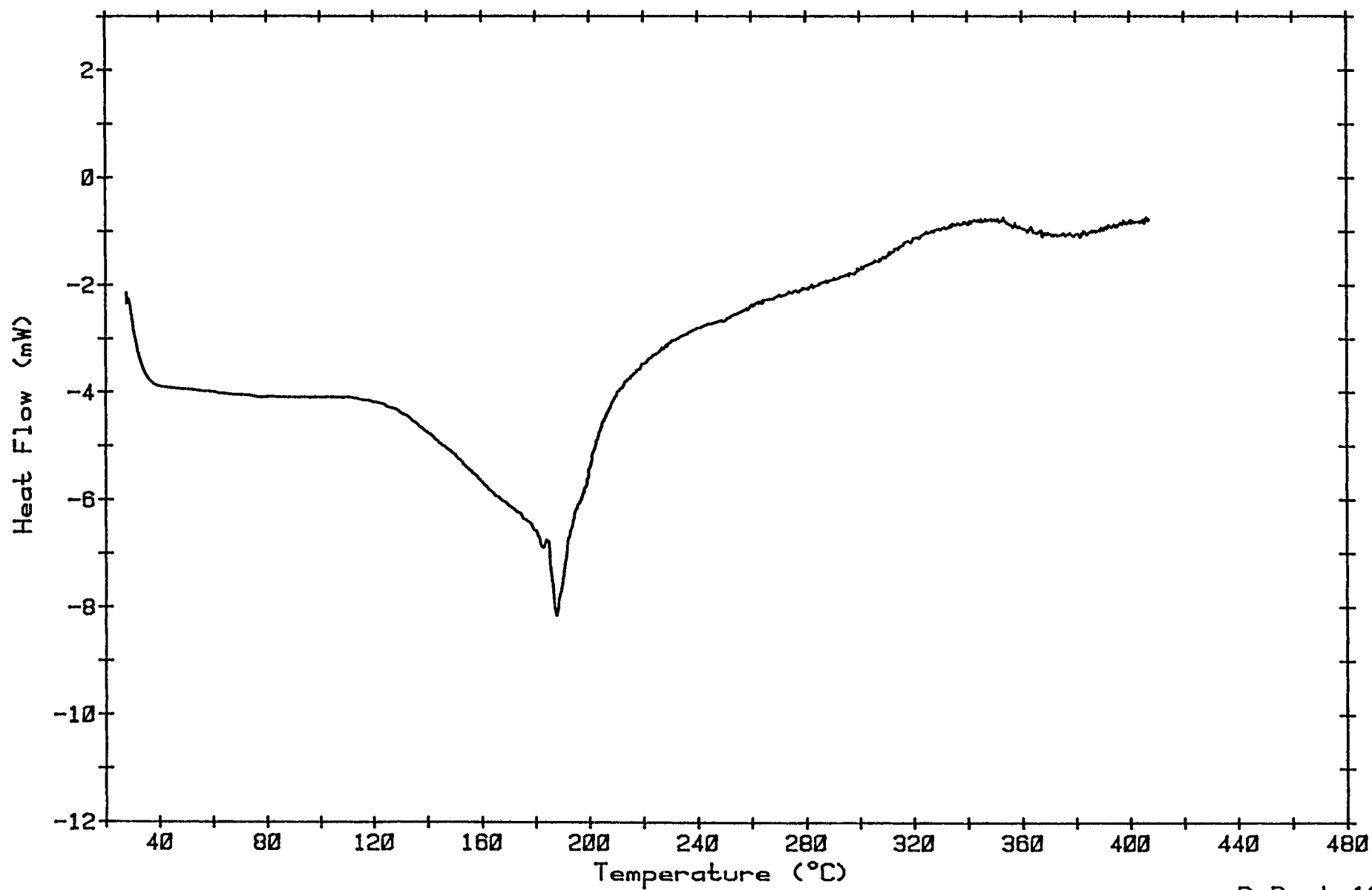


FIG. 3-28  
DSC OF PMR-15 STAGED .5 HR/120 C.

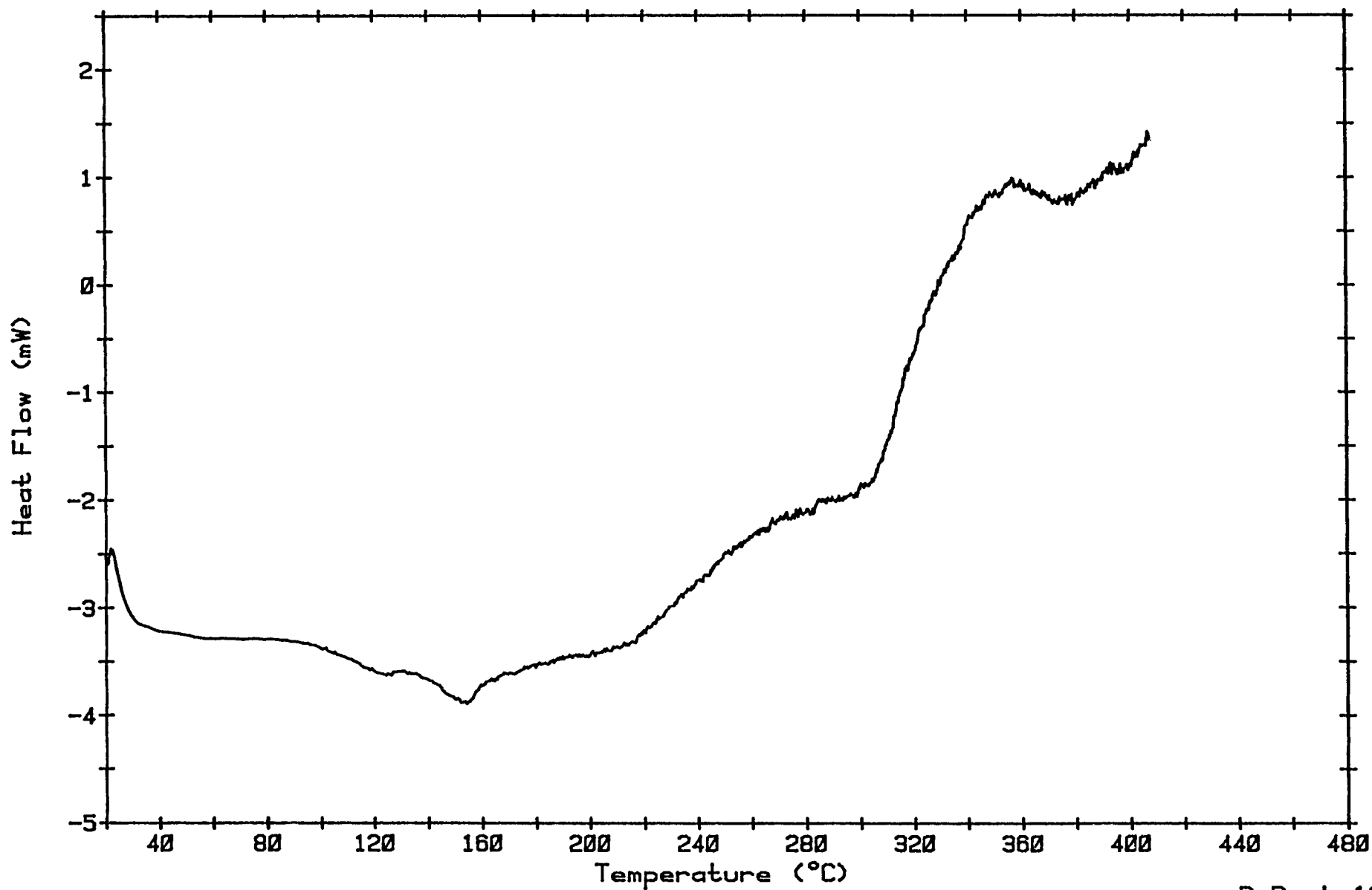


FIG. 3-29  
DSC OF LARC 160/22 UNSTAGED

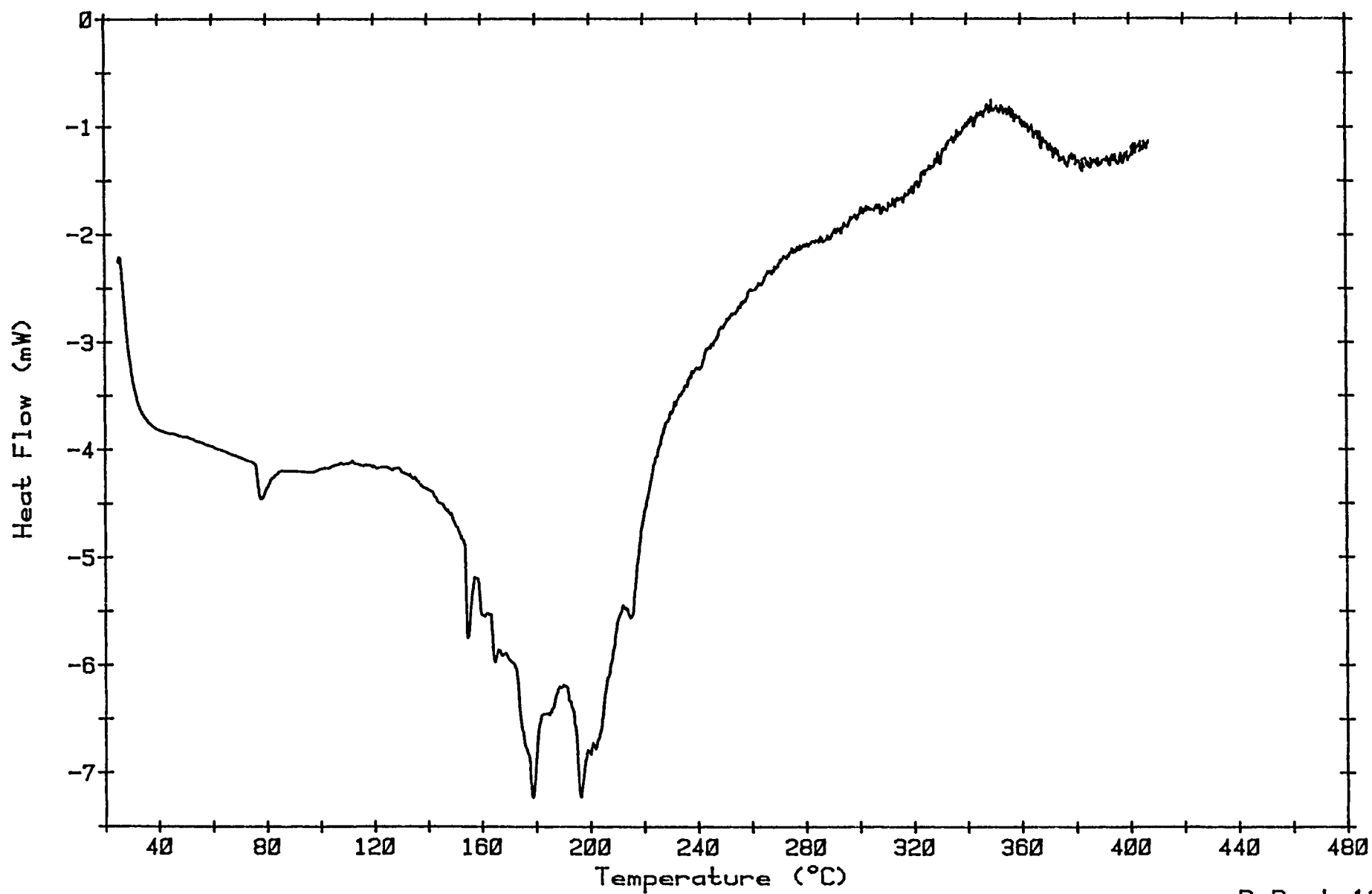


FIG. 3-30  
DSC OF LARC 160/22 STAGED .5 HR/120 C.

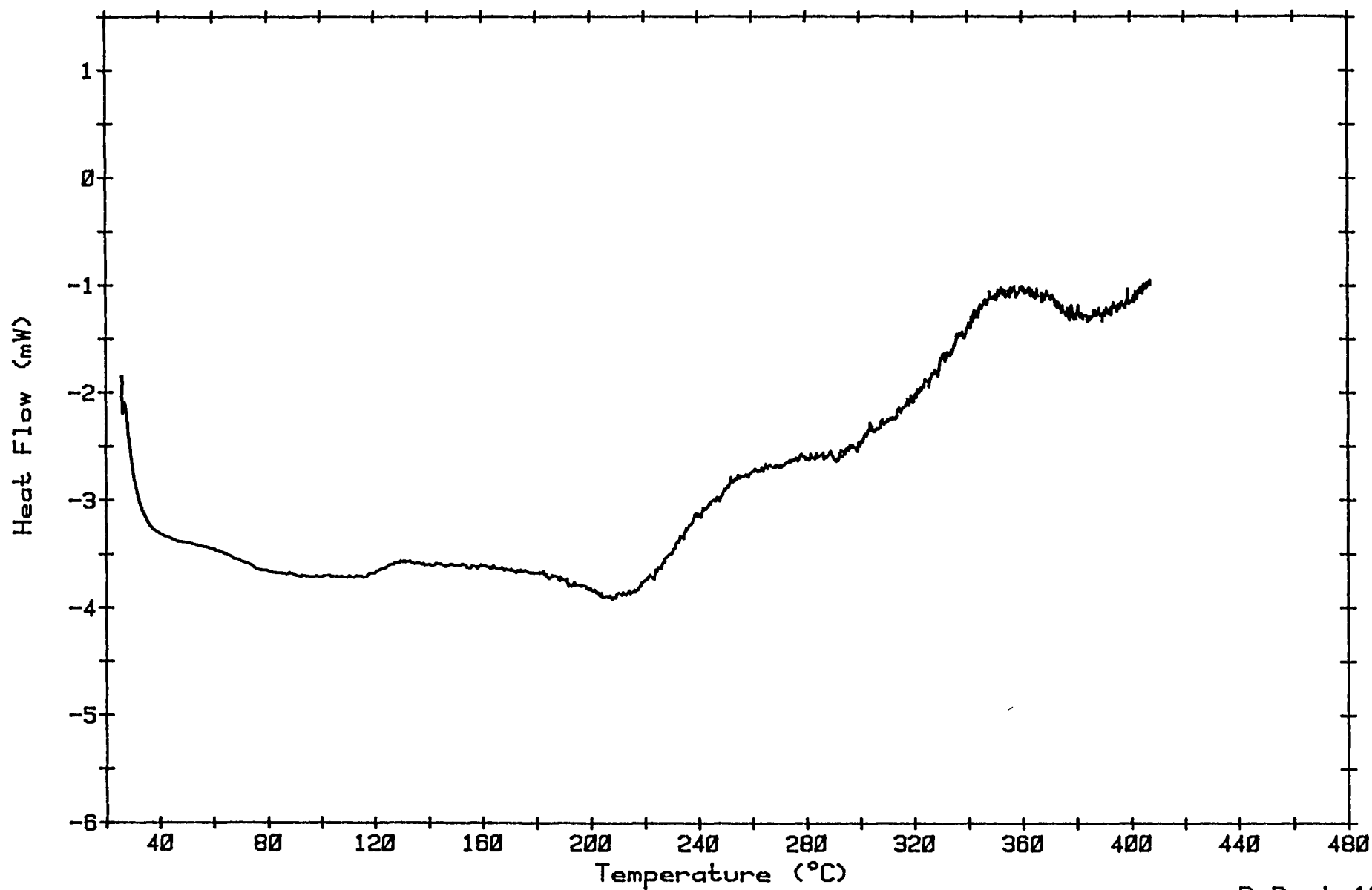


FIG. 3-31

DSC OF LARC 160/103 UNSTAGED

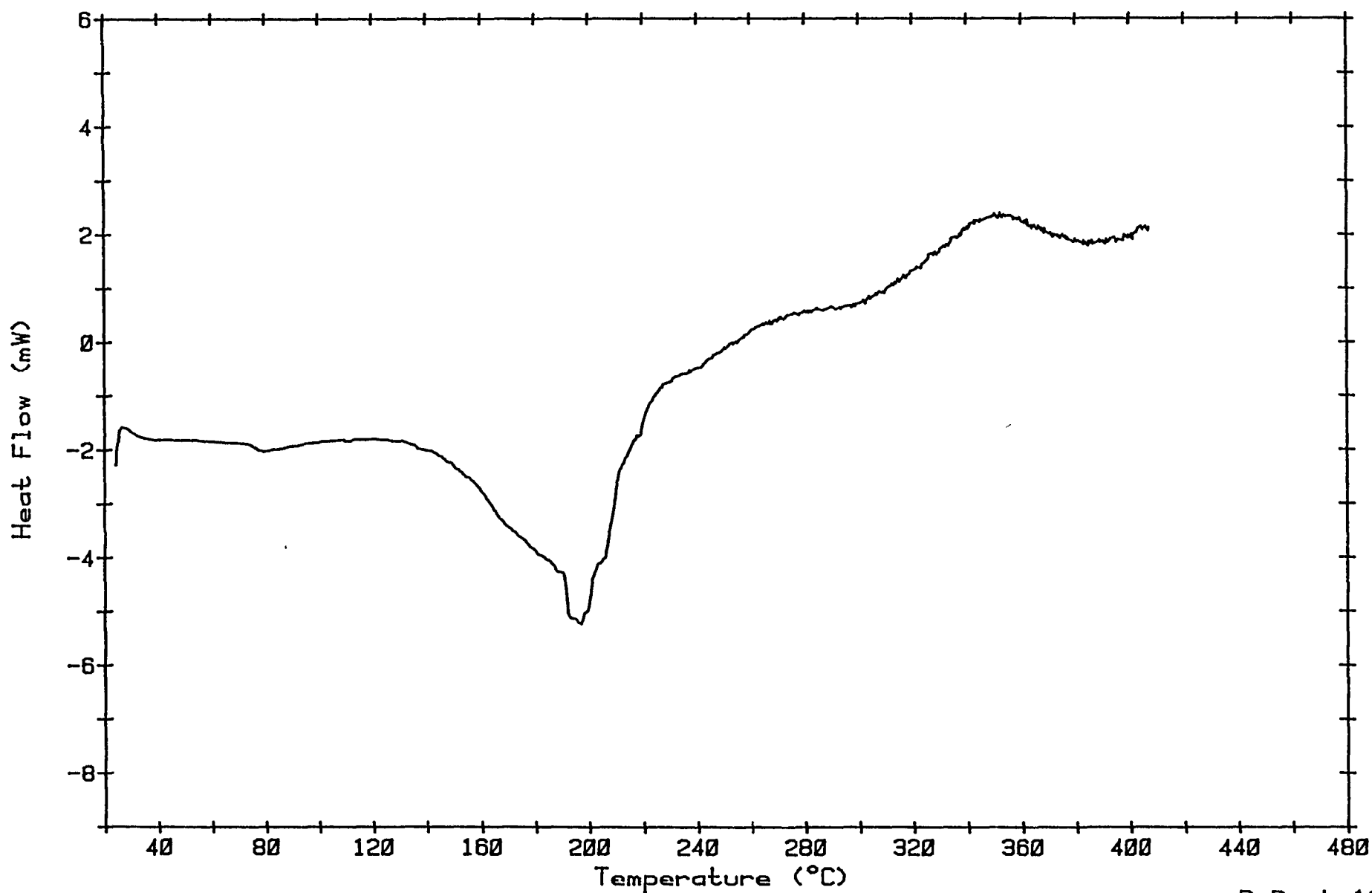


FIG. 3-32  
DSC OF LARC 160/103 STAGED .5 HR/120 C.

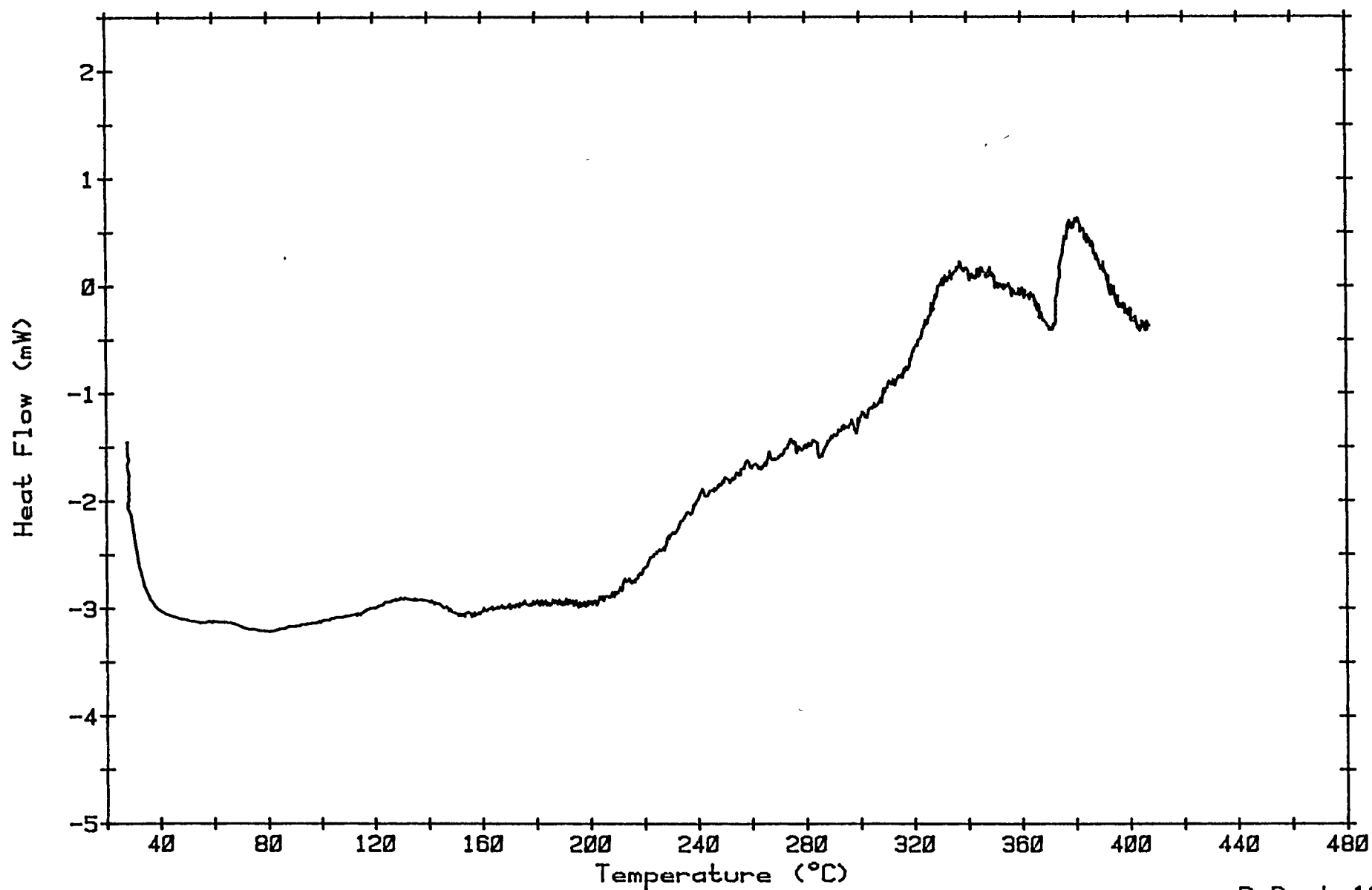




FIG. 3-33  
DSC OF PMR-15 UNSTAGED

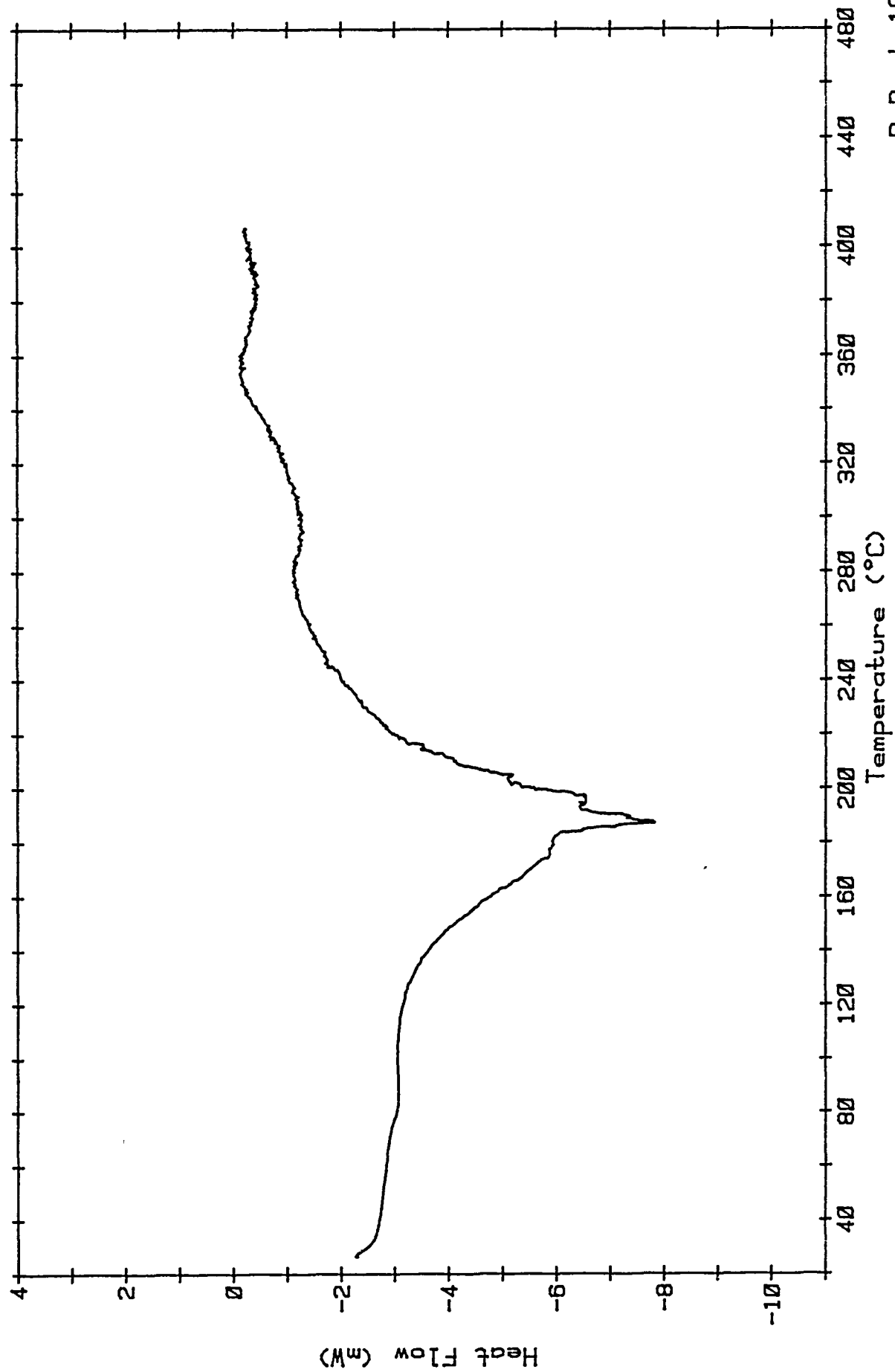
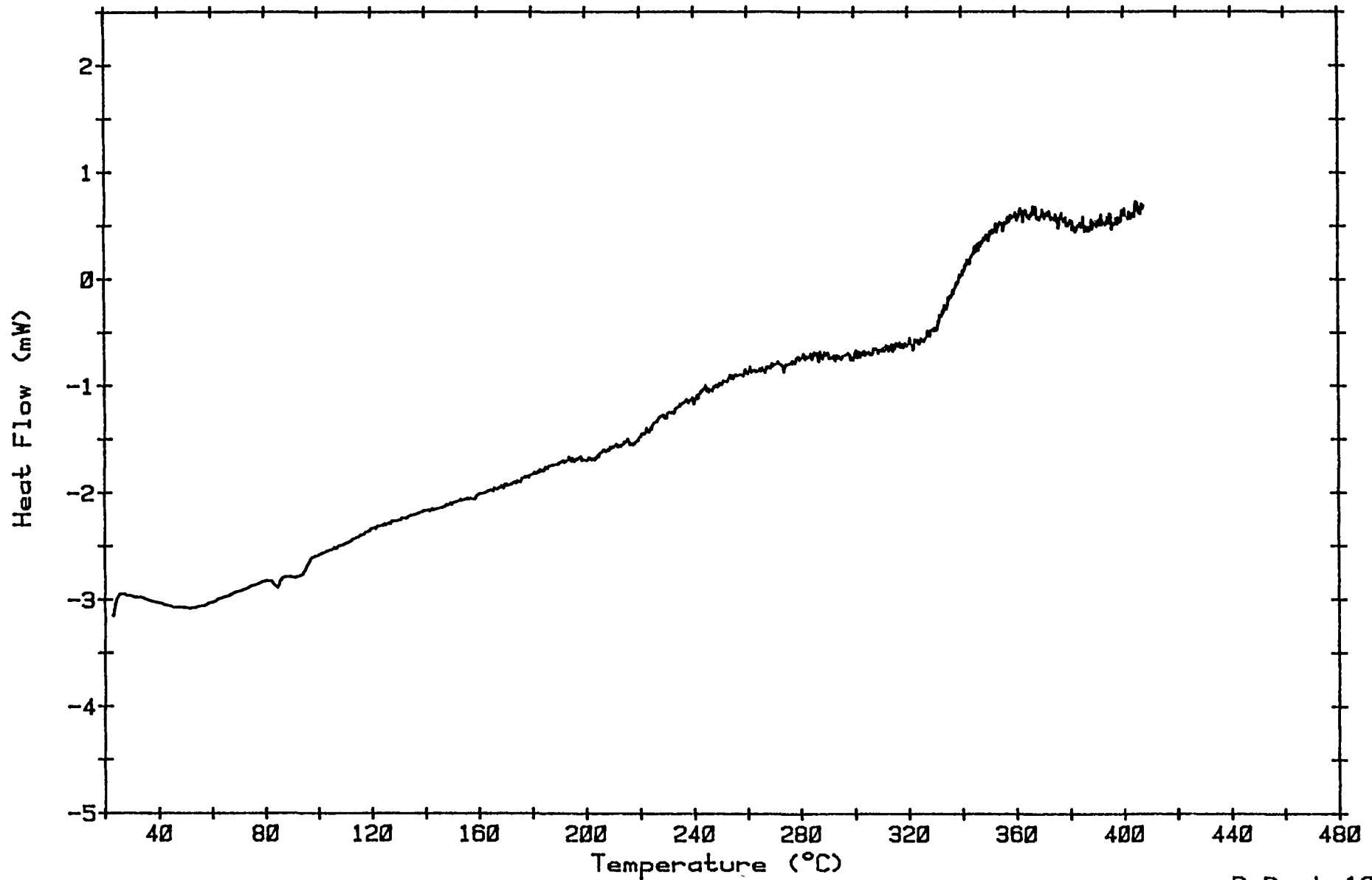


FIG. 3-34  
DSC OF PMR-15 STAGED .5 HR/120 C.



The staged powders were then molded at 320°C, 0.83 MPa pressure for 1 hour. Satisfactory moldings were produced, samples were machined for both TMA and rheological testing.

TMA curves were run on the moldings but failed to provide firm Tg data in the case of Curithane LARC 160. The AP-22 version shows a Tg of 326°C. Several transitions occur in the Curithane version. Curves were repeated with similar results. One interpretation would assign a Tg of 400°C for Curithane LARC 160. This interpretation agrees with rheological data presented in the following section. (See Figures 4-9 and 4-10.)

#### 4.0 RHEOLOGICAL STUDIES

##### 4.1 PISO<sub>2</sub> Studies

Prior to the synthesis of the LARC 160 resin, a sample of a thermoplastic polyimidesulfone resin designated PISO<sub>2</sub> was furnished by NASA for rheological characterization. It has a reported Tg in the 235-240°C range and can be molded at 250°C under 1.38 MPa pressure. The attempts to measure the viscosity of PISO<sub>2</sub> were, however, unsuccessful. Temperatures as high as 320°C were used to form in-situ samples in the rheometer but adequate pressure could not be generated. Consequently, a molding fixture was fabricated so that a sample could be molded between disposable Rheometrics discs in a heated-platen press. Temperatures ranging from 260 - 288°C and pressures from one to 110 MPa were explored. Flow was not achieved until a combination of 288°C and 110 MPa were used. However, the film was not amenable to Rheometrics characterization since it could not be remelted in the instrument and it would not adhere to the plates. No further work was scheduled on the PISO<sub>2</sub> system because of these difficulties.

##### 4.2 LARC 160 from Prepreg Samples

In order to begin rheological studies on LARC 160 prior to the synthesis of the LMSC panels, a sample of commercial prepreg was used. As a LARC 160 panel finished the imidization step, the resin flash was broken off for our sample. The flash was pulverized with a mortar and pestle and then quickly heated to between 238 and 250°C in the Rheometrics sample cavity. At that time a programmed heating rate was initiated. A check for reproducibility was first conducted at a heating rate of 4°C/min. The three types of curves encountered are shown in Figure 4-1. Three runs closely paralleled curve II while curves I and III were unique. The range in these responses was clearly unacceptable. Contributing factors were residual volatile content and non-uniform staging within the rheometer. A few bubbles were found between the parallel plates of the rheometer after separation at the end of test.

FIG. 3-35  
TMA OF LARC 160 W/AP-22

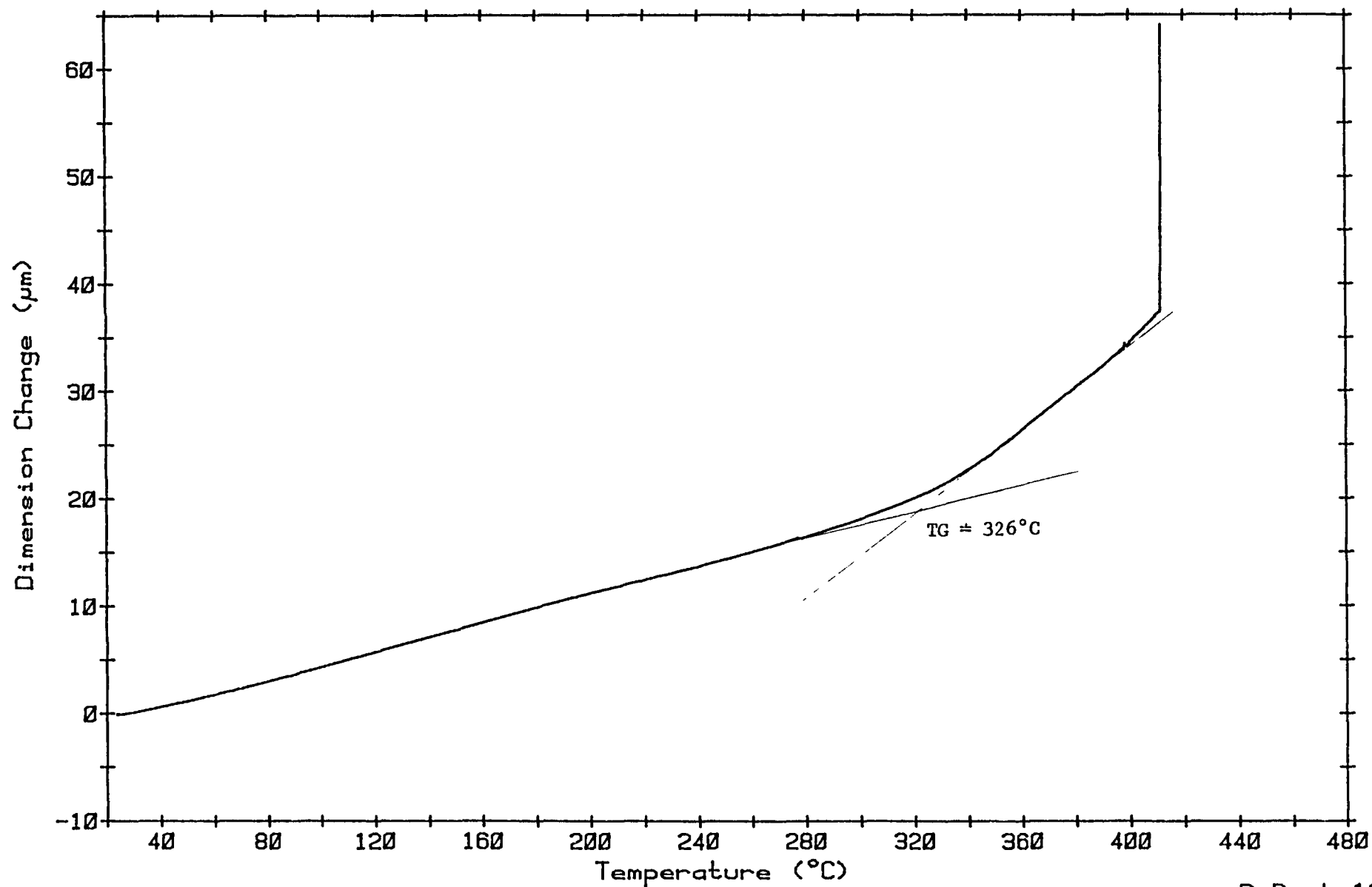


Figure 3-35

FIG. 3-36  
TMA OF LARC 160 CURITHANE 103

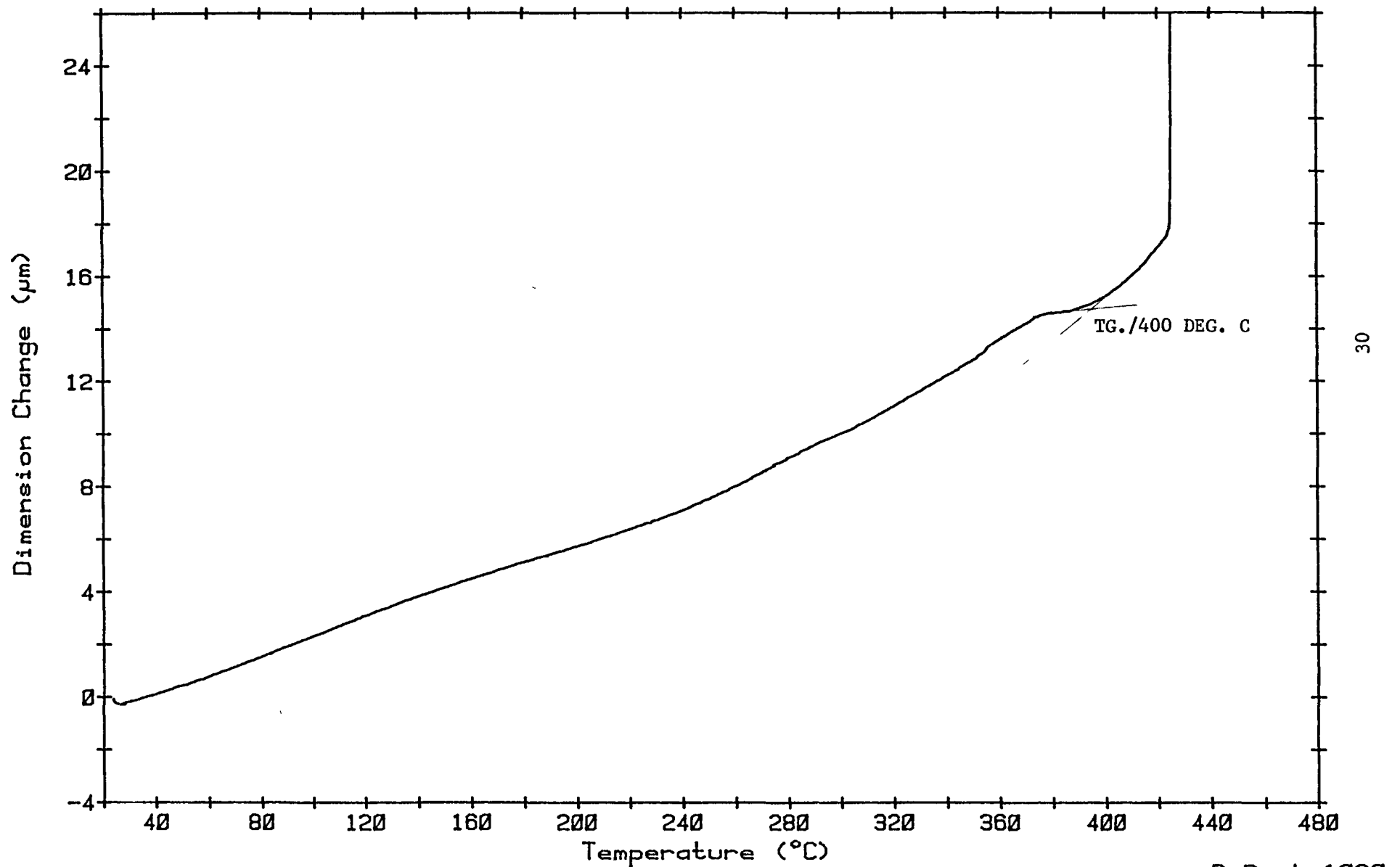


Figure 3-36

The effect of heating rate was investigated in the range between 2 and 4°C/min. These rates bracket the 2.8°C/min. appropriate for autoclave curing. The viscosity is plotted as a function of temperature for 2 and 4°C/min in Figure 4-2. A minimum viscosity of 1700 poise is found at 272°C when heated at 2°C/min. This minimum decreases to 580 poise at 287°C when the rate is increased to 4°C/min. Based on the reproduction experiments these figures must be regarded as approximate. However, the trend is what one should expect.

Another experiment of interest addressed the introduction of an isothermal hold for pressure application. Temperatures of 260°C and 275°C were explored and the results are shown in Figure 4-3. It is interesting to compare the 2°C/min. viscosity increases with and without a hold at 275°C. Using the viscosity at 275°C as a reference, a ten fold increase in viscosity occurred after 16 minutes with no hold and 13 minutes with one. This result was rather surprising and suggests that the introduction of a temperature dwell for pressurization may be counter-productive.

#### 4.3 LARC 160 Resin Studies

After the initial batches of LARC 160 were prepared, it was decided to concentrate the studies on these material systems. A study was conducted to evaluate the effect of volatile content on viscosity. Results are shown in Figures 4-4 and 4-5 where  $\eta^*$  and  $\tan \delta$  are shown as a function of time. The resin is LARC 160 with Curithane 103 and the heating rate was 2°C/min. As synthesized, the initial viscosity at RT was 62 poise and the minimum viscosity at 87°C was 9.2 poise. The volatile content was 48%. After two hours of drying at 50°C resulting in a volatile content of 27%, the RT viscosity increased to 3400 poise and the minimum viscosity at 85°C was 39.7 poise. Note, too, the appearance of an initial peak in  $\tan \delta$  which indicates resin softening. Measurement of  $\tan \delta$  is expected to be useful when correlating viscosity measurements to dielectric measurements for the purpose of cure monitoring. The second peak in  $\tan \delta$ , in the vicinity of 131°C (55 min.), can be associated with resin hardening caused by imidization. The scatter in both curves is the result of bubble formation within the sample cavity as the residual ethanol and condensation by-products boil off.

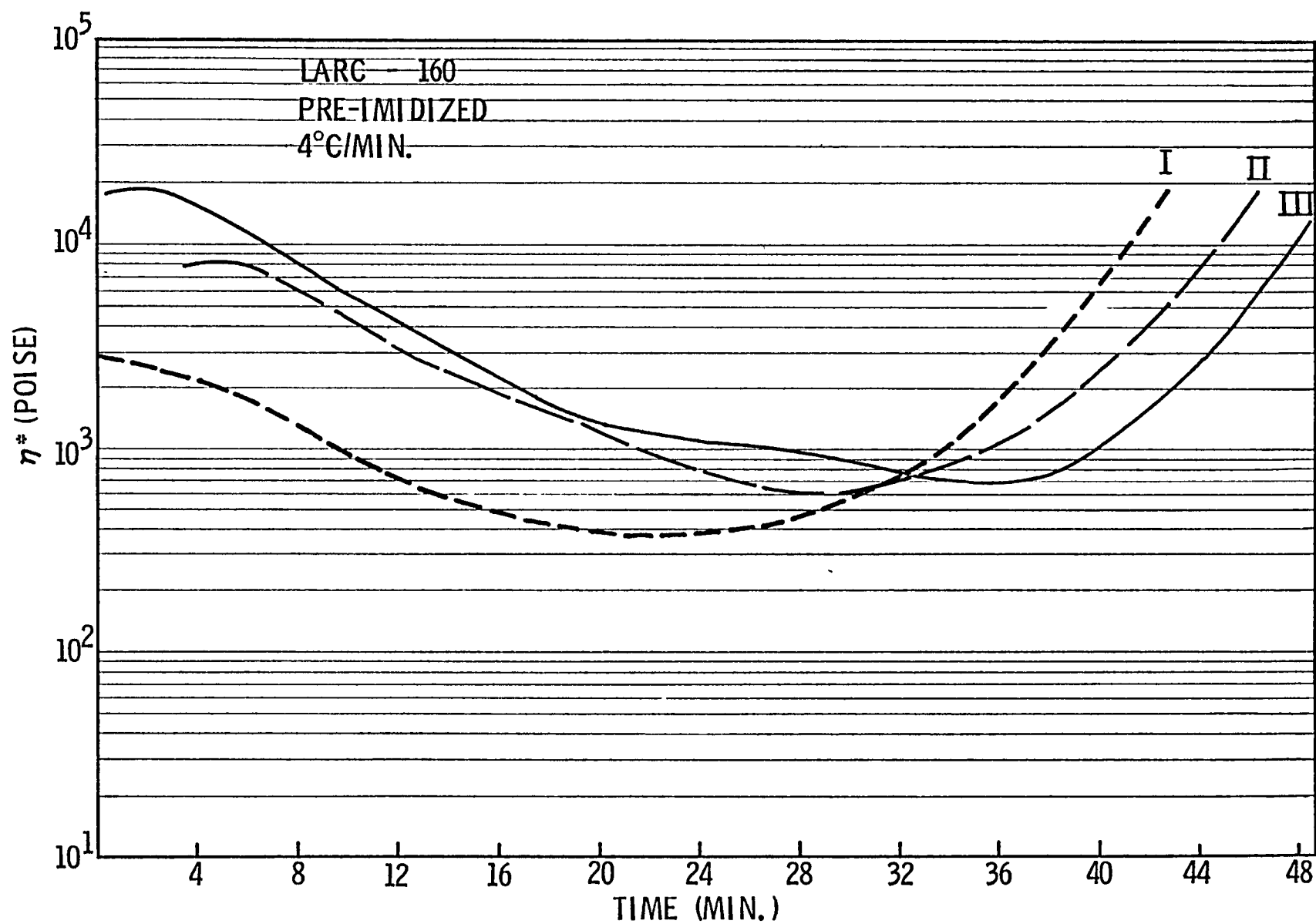


FIGURE 4-1 THREE TYPES OF VISCOSITY CURVES

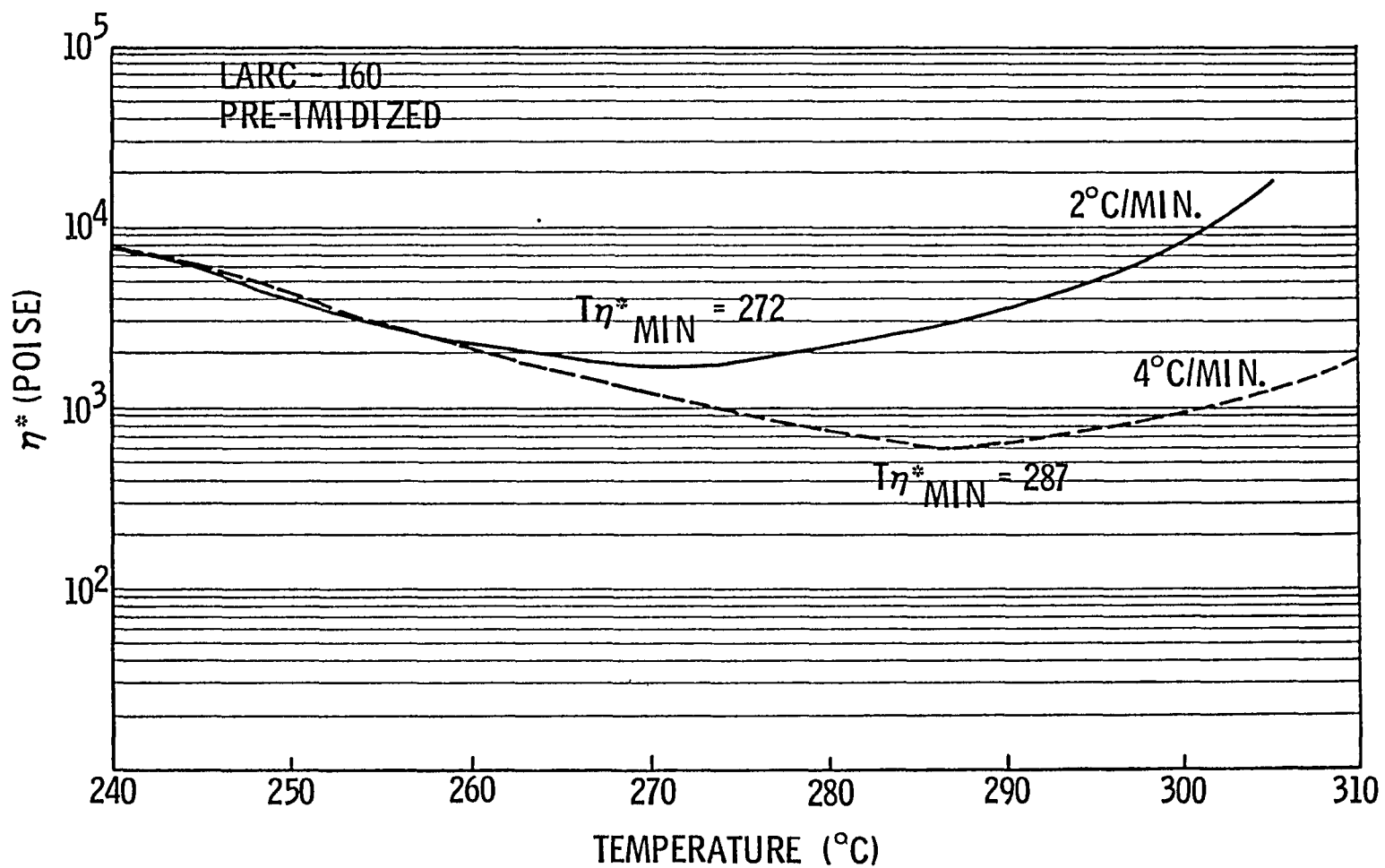


FIGURE 4-2 EFFECTS OF HEATING RATE ON VISCOSITY



A similar curve of  $\eta^*$  vs  $t$  for an as-synthesized sample of LARC-160 with Jeffamine AP-22 is shown in Figure 4-6. A RT viscosity of 66 poise is similar to that of LARC 160 with Curithane 103, but the minimum viscosity at 84°C (13.6 poise) does not get as low as LARC 160 with Curithane 103 (9.2 poise). Also, the  $\tan \delta$  imidization peak occurs at 124°C which is 7°C lower than that for the Curithane 103 version of LARC 160. Thus, it appears that substituting Curithane 103 for Jeffamine AP-22 causes the resulting LARC 160 to soften more and perhaps to react slower during the imidization reaction. Furthermore, the imidized resin appeared to have a higher viscosity in the case of the Curithane 103 version of LARC 160.

The rheological behavior of preimidized samples of LARC 160 and PMR 15 (ethanol solution) were next compared. The data was gathered on samples which were oven imidized at 121°C for 60 minutes prior to characterization. After imidization, samples were pulverized and desiccated. Prior to measurement, samples were further dried in a desiccated vacuum oven (RT/380-510 mm Hg) overnight.

In order to form a sample in the environmental chamber of the rheometer, the chamber is preheated to 200°C and a pre-weighed amount of imidized resin (fine powder) is introduced between opened parallel plates. The chamber is then closed and when the indicated temperature again reaches 200°C a sample is formed by closing the plates to a predetermined gap (0.6mm). The chamber is again opened and excess resin is removed from the edges of the plate. The chamber is reclosed and heating is resumed when the chamber reaches 200°C.

Complex viscosity as a function of temperature is shown in Figure 4-7 for LARC 160 (AP 22 and Curithane 103 versions) and PMR 15 (ethanol solution) at heating rates of 2 and 4°C/min. There appear to be distinct differences between all of the resins. The greatest difference was between the two types of LARC 160. Because of the greater amount of 4,4'-MDA in Curithane 103, one might logically expect this version of LARC 160 to have a higher minimum viscosity than its AP-22 counterpart. However, the data shows the opposite. Furthermore, if the AP-22 version of LARC 160 is compared to earlier data obtained from preimidized LARC 160 prepreg the viscosity profiles of the two resins are significantly different. The resin from the prepreg reaches a minimum viscosity in the neighborhood of 400 poise at 292°C as compared to around 7,000 poise at 250°C for freshly synthesized resin. Although the

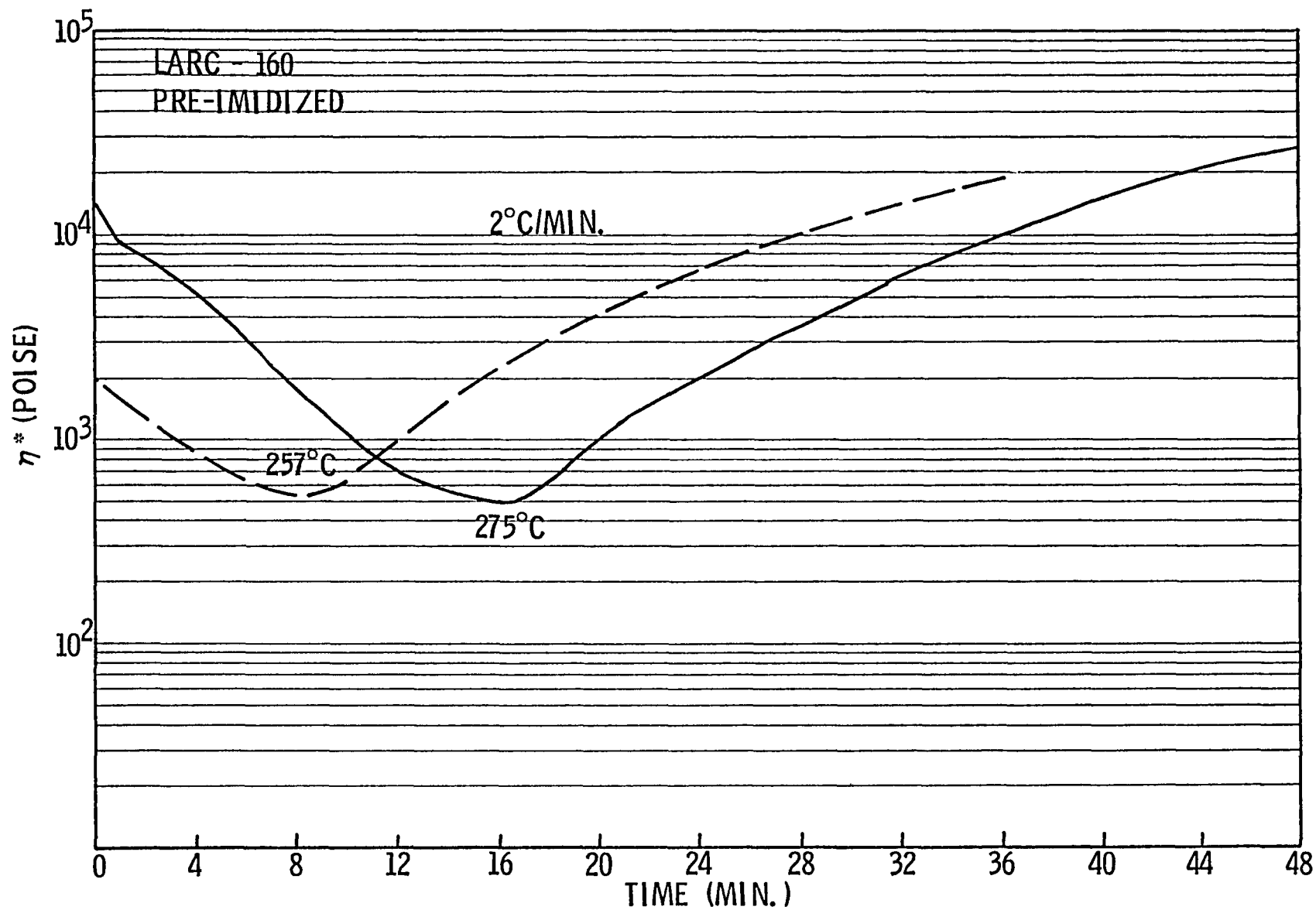


FIGURE 4-3 EFFECTS OF ISOTHERMAL HOLD TEMPERATURE ON VISCOSITY

heating rates were the same, i.e. 4°C/min., the prepreg resin was scanned and started at 239°C while the current material resin was scanned from 200°C. The additional time at higher temperatures tends to explain the observed differences and also presents another problem. The viscosity measured in a characterization run might not reflect the true viscosity during a process. It clearly points out the need for parallel heat histories of samples being compared.

Note that an improved viscosity characterization procedure would be desirable to eliminate the initial peak in complex viscosity during the first 10-20 minutes of a run. The resin is not very fluid at 200°C. The lower temperature was used to minimize any reactions during sample formation and hence give better reproducibility. This higher initial viscosity requires a low shear stress and low shear rate because of the transducer limitations. However, the deflection of the transducer shaft must exceed 0.001 of the radius in order to give reliable results. The shear strain of 3 used to generate the data in Figure 4-7 was later found to be slightly less than required by calculation ( $\gamma = 5$ ). The data is thus questionable. The effect of shear strain was examined in subsequent tests and the data appears in Figure 4-8.

For the AP-22 version of LARC 160, shear strains of 3, 5, 10 and 50 were examined. A starting temperature of 230°C was required to get the initial viscosity low enough to accept the higher shear strains. The data shows a scatter band but no systematic variation as a function of shear strain. The only large difference occurs in the case of  $\gamma = 3$ . Similar data for the Curithane 103 version of LARC 160 at shear strains of 3, 10 and 50 are also shown in Figure 4-8. In this case, the largest difference occurs in the case of  $\gamma = 50$ . It would appear that a shear strain of 10 might be the best choice. Despite the scatter, it is clear that in all cases the Curithane 103 version of LARC 160 has a lower minimum viscosity in the process critical range as compared to AP 22.

The 500 gram batches of LARC 160 (AP-22 and Curithane 103) were next synthesized. While initial chemical characterization was being carried out, (see Section 3) we prepared neat resin specimens for solid state testing. Note that the additional staging required to produce resin molding from the Curithane 103 LARC 160 (Section 3) is consistent with the lower viscosity indicated by the Rheometrics curves.

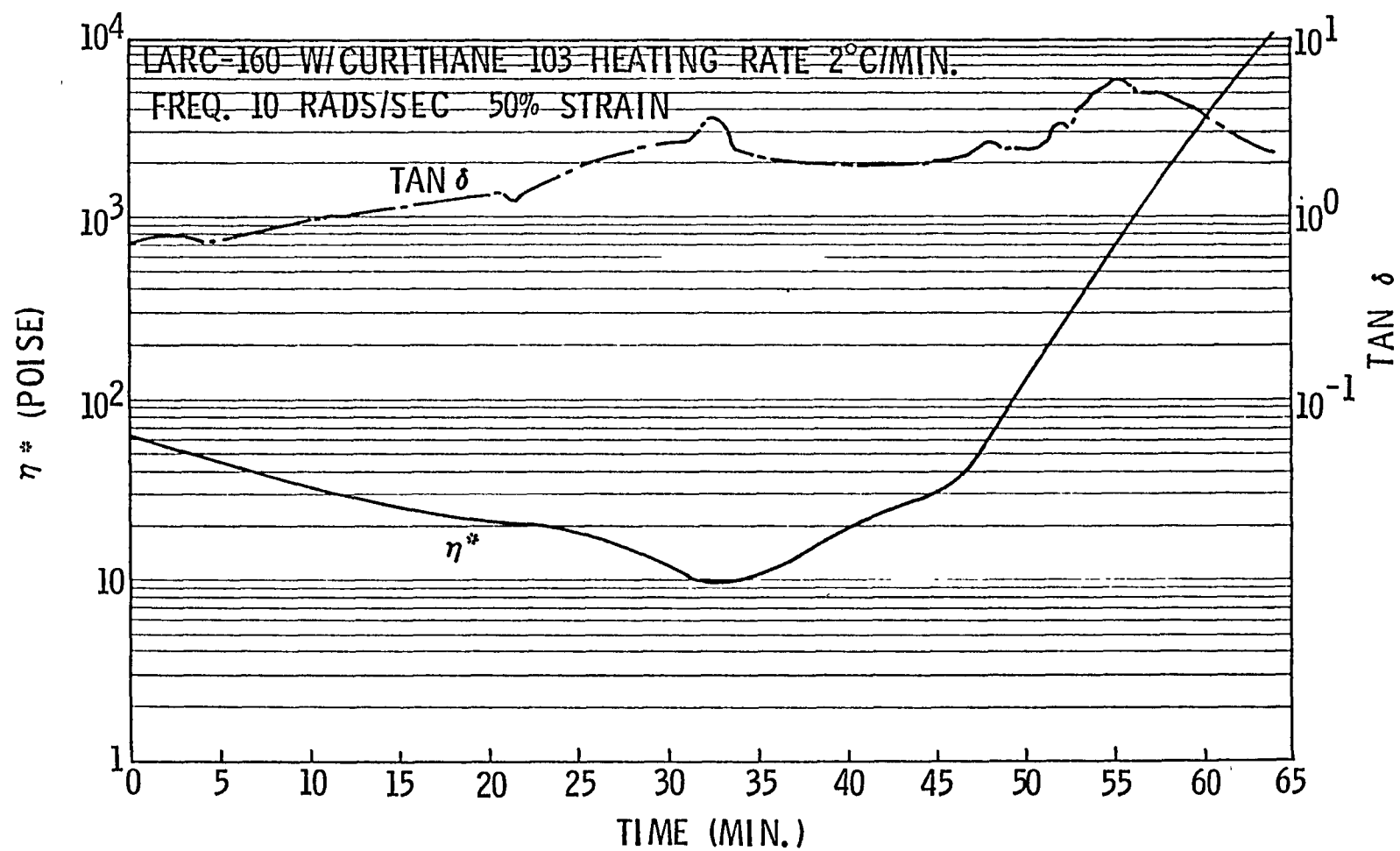


FIGURE 4-4 EFFECTS OF VOLATILE CONTENT ON VISCOSITY

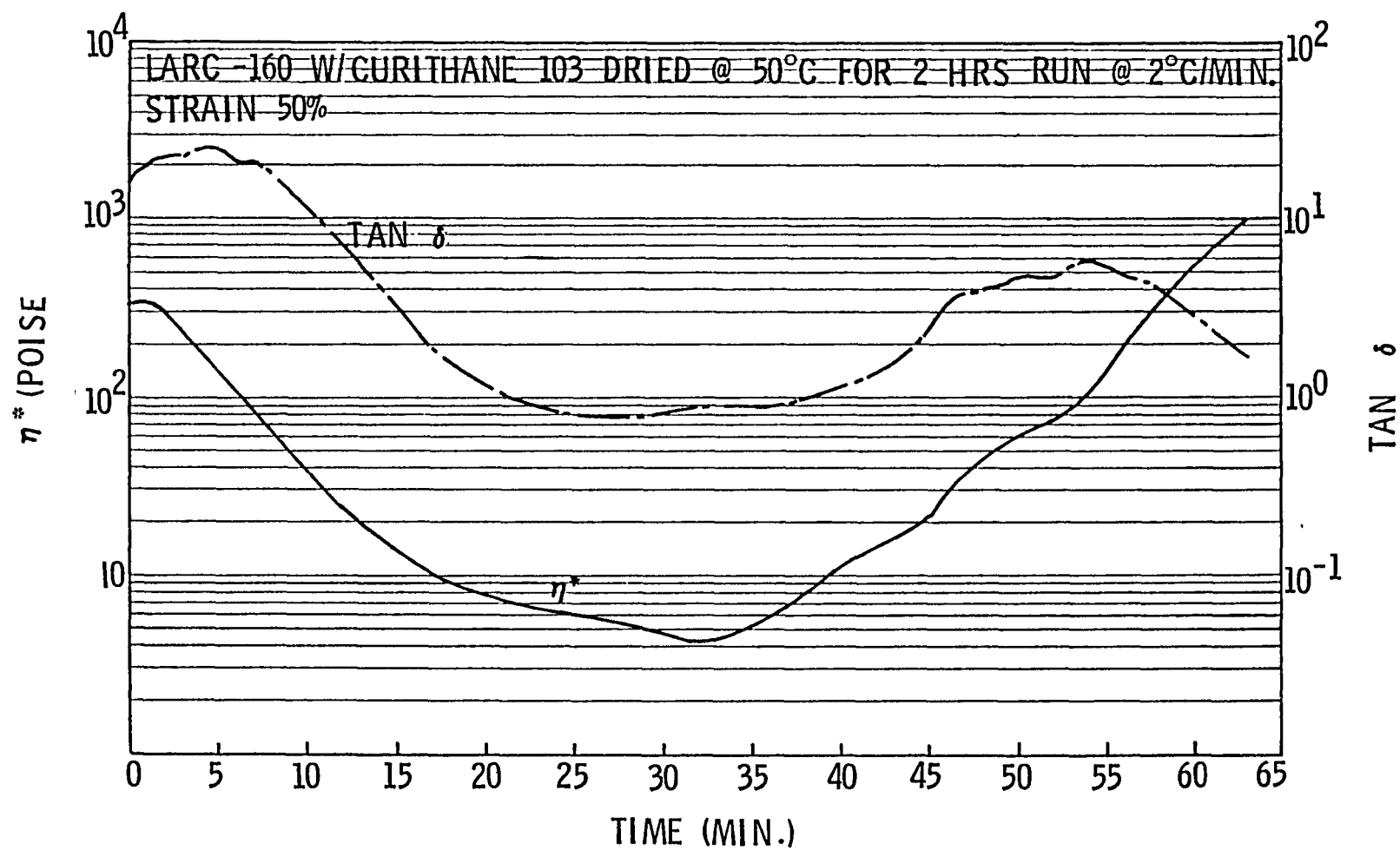


FIGURE 4-5 EFFECTS OF VOLATILES ON VISCOSITY

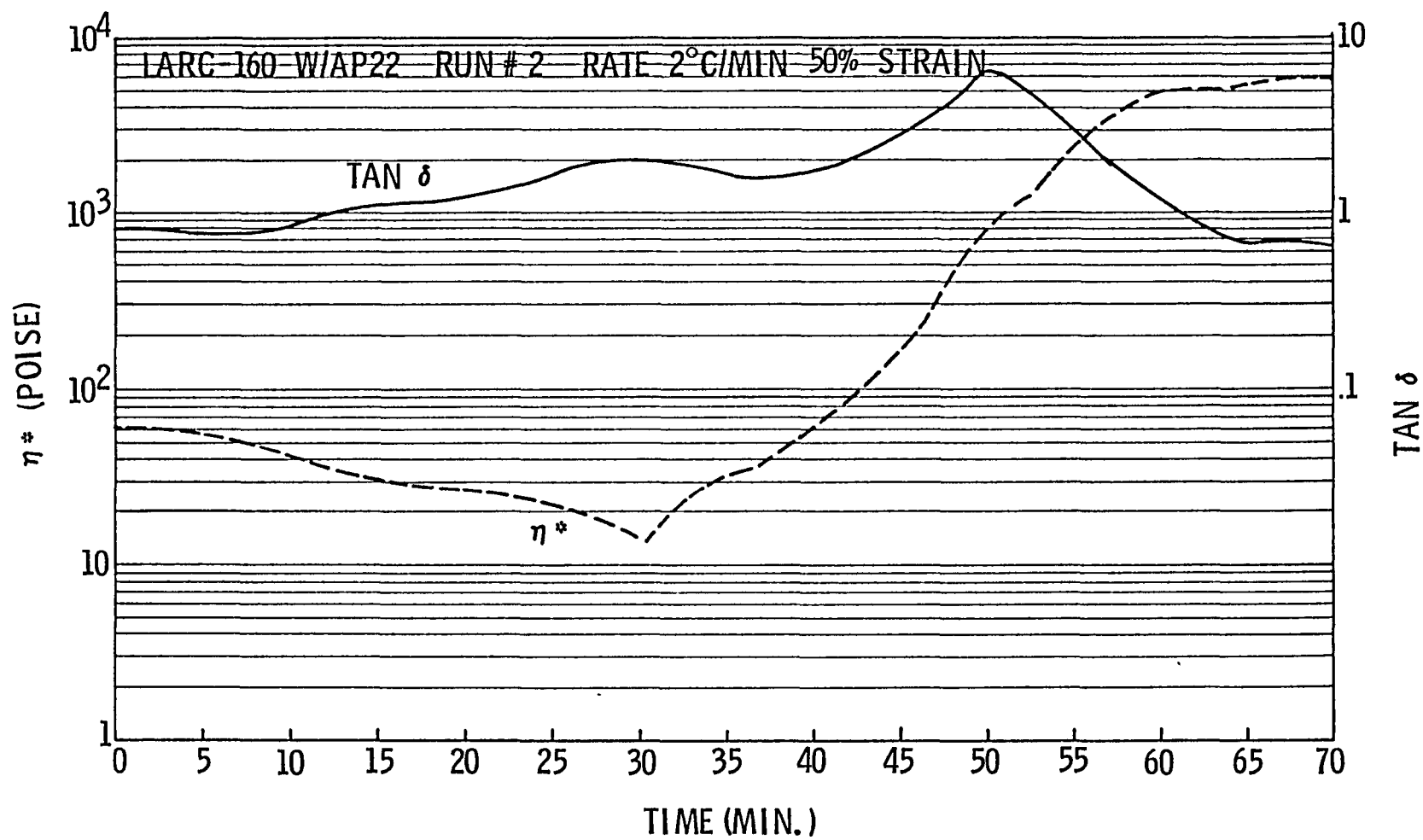


FIGURE 4-6 COMPLEX VISCOSITY VS TEMPERATURE

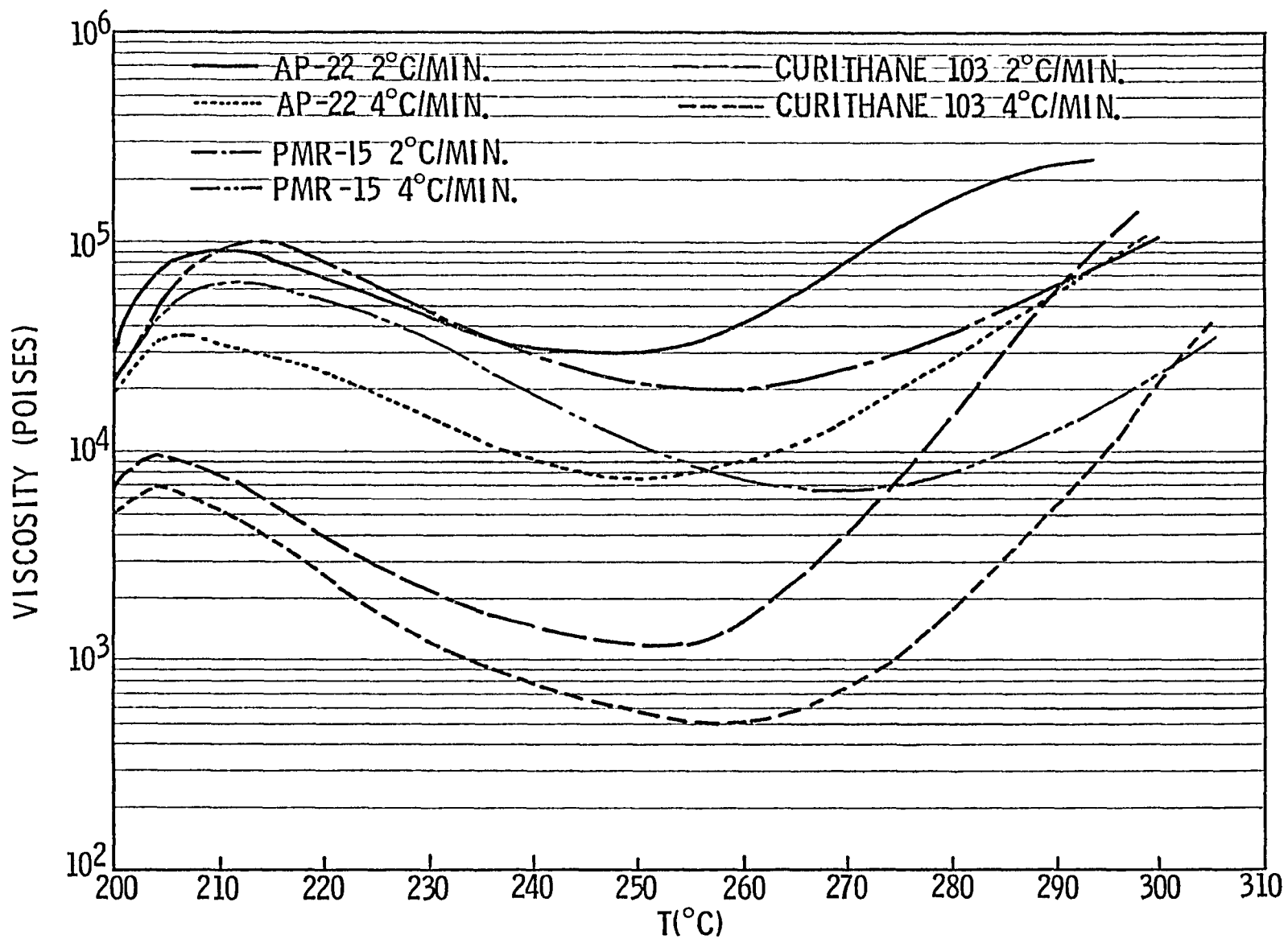


FIGURE 4-7 COMPLEX VISCOSITY VS TEMPERATURE

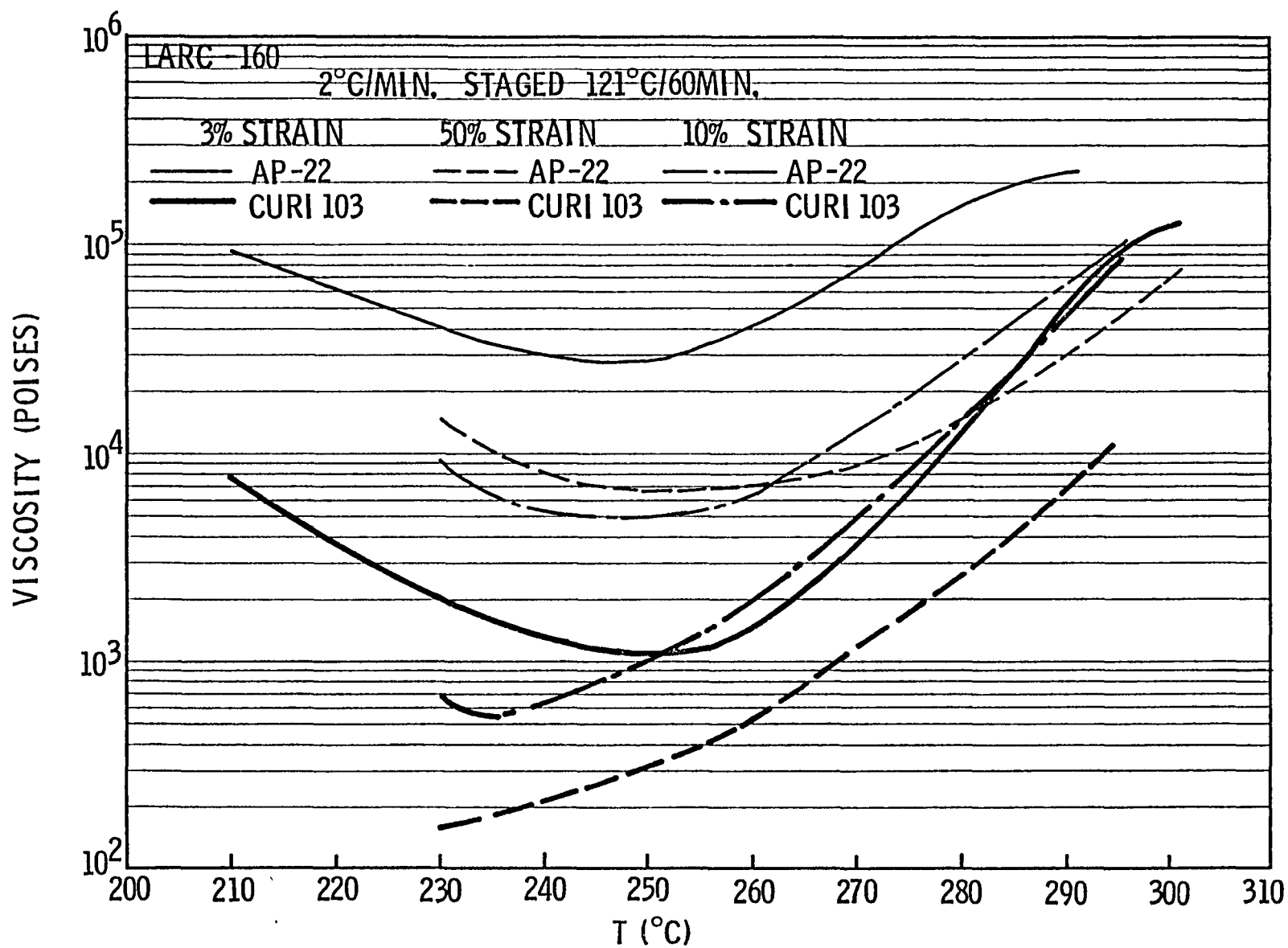


FIGURE 4-8 EFFECT & OF SHEAR STRAIN



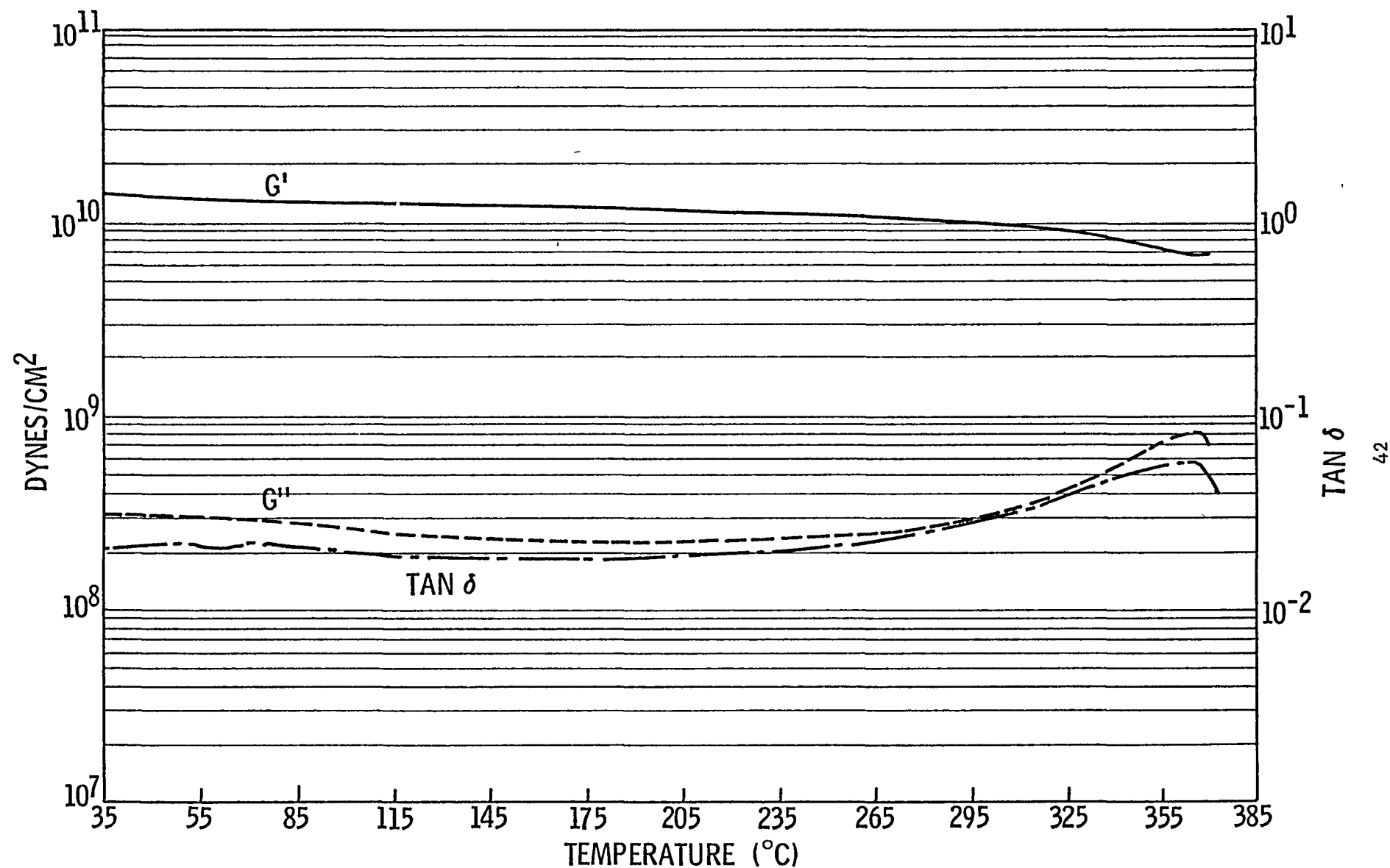


FIGURE 4-9 LARC 160 W/AP-22 (NEAT RESIN CASTING)

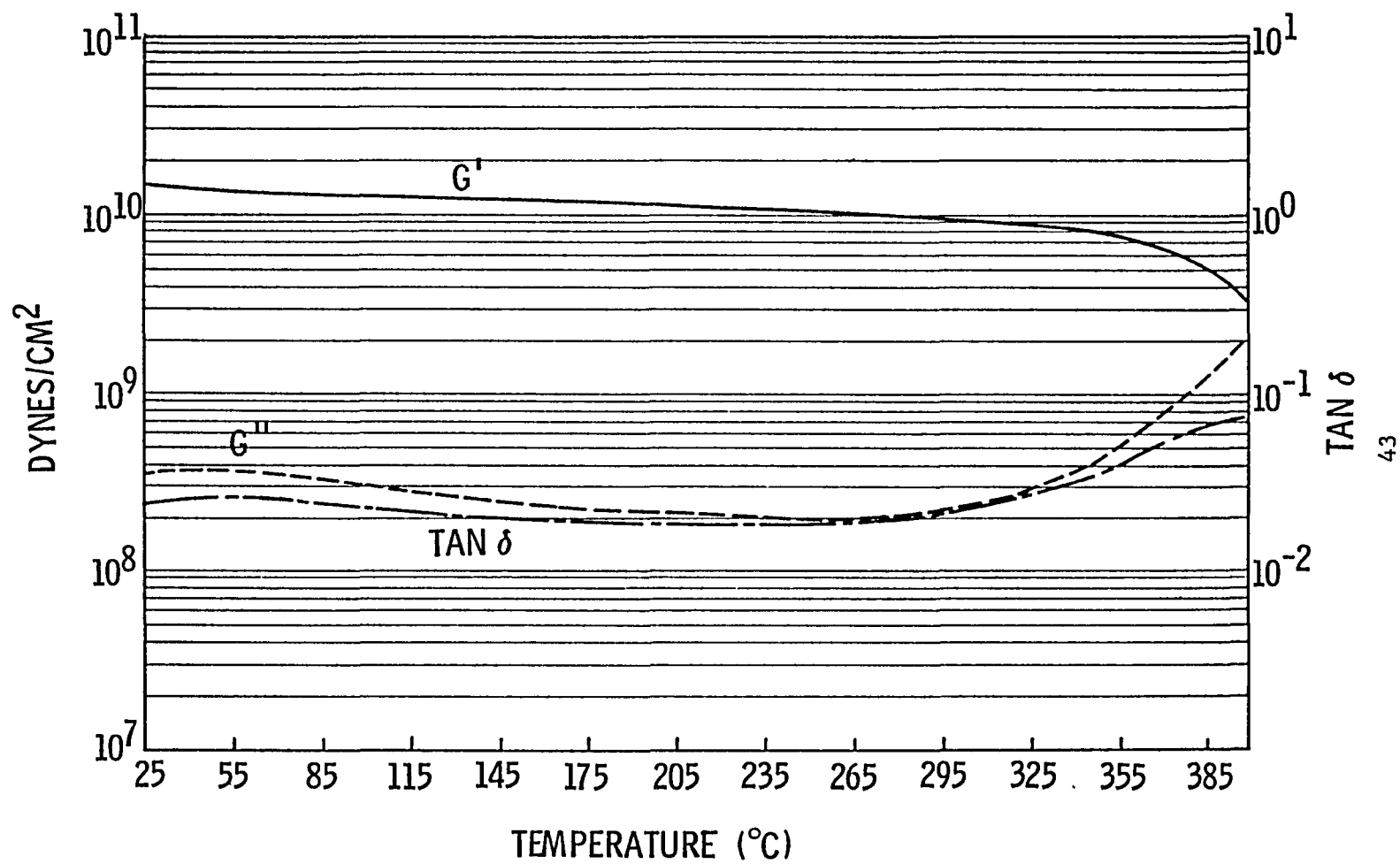
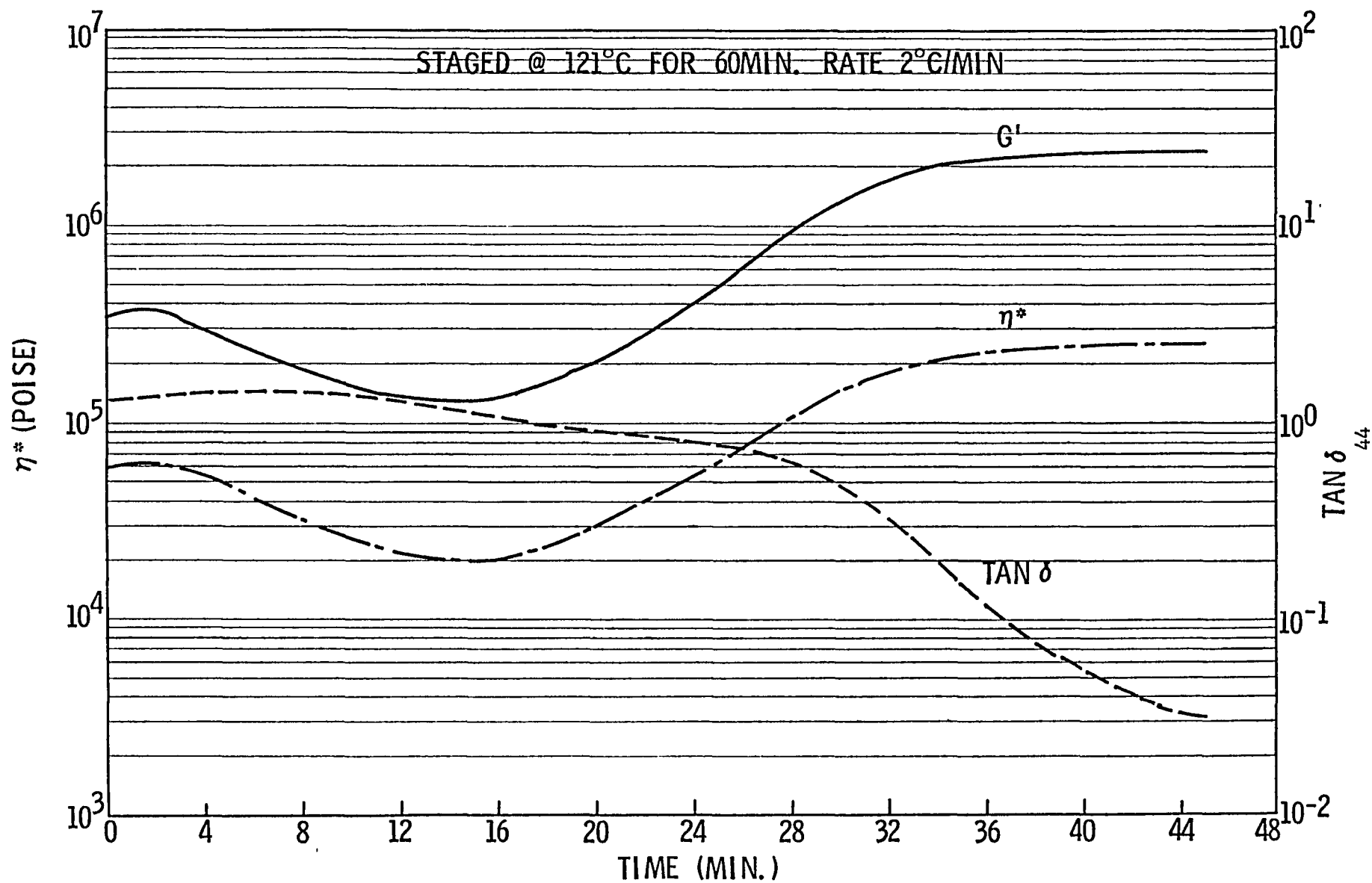


FIGURE 4-10 LARC 160 W/CURITHANE 103 (NEAT RESIN CASTING)



4-11 VISCOSITY VS TIME, LARC 160/AP-22

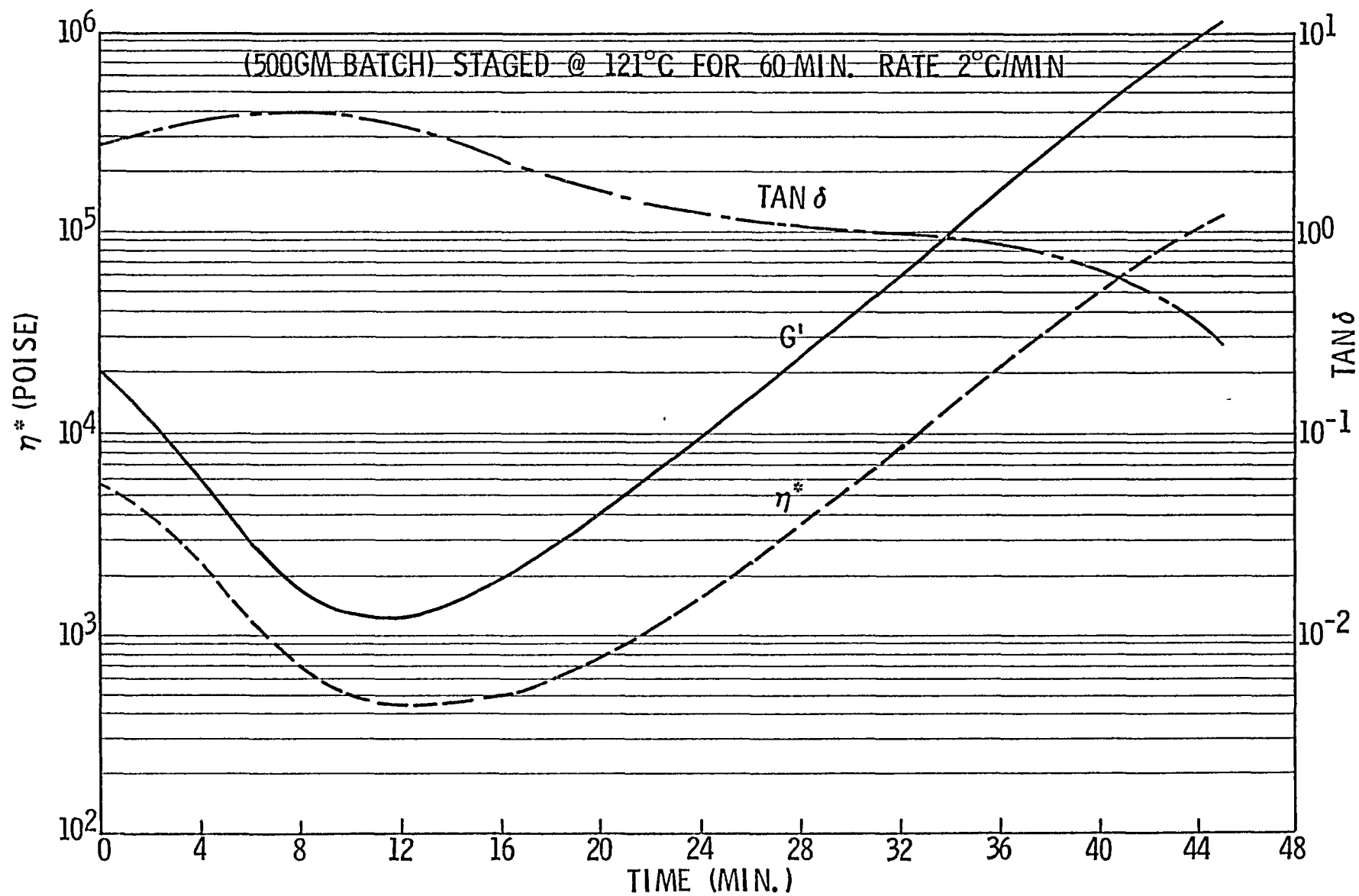


FIGURE 4-12 VISCOSITY VS TIME, LARC 160/CURITHANE 103

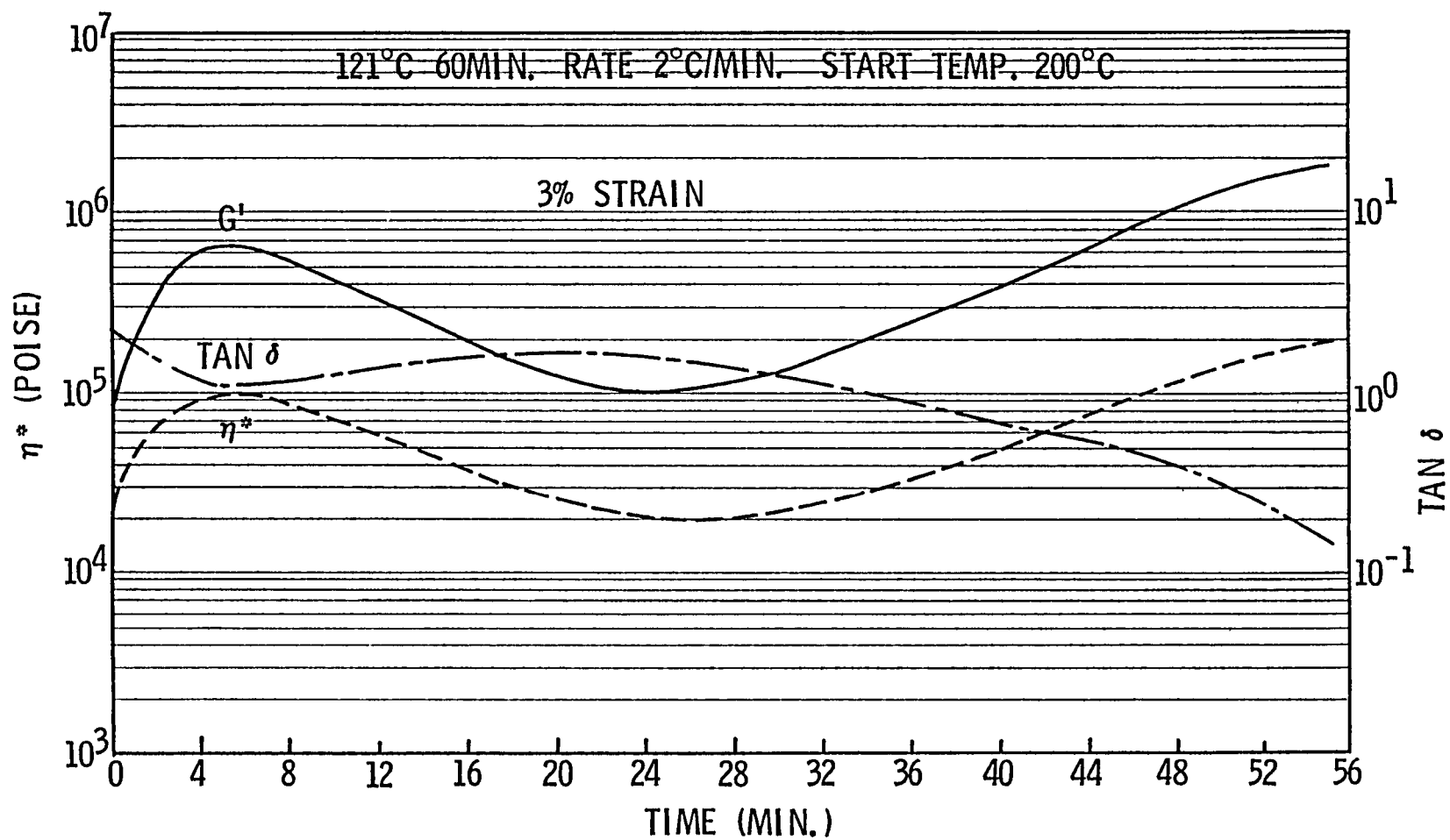


FIGURE 4-13 PMR-15 RESIN VISCOSITY CURVE

Solid state data was obtained. The peak in  $\tan \delta$  occurred at 367°C for the AP-22 LARC 160, while the curve went off-scale (at 397°C) for the Curithane 103 version. Figures 4-9 and 4-10 show solid state curves for the two LARC systems. This data is consistent with earlier TMA results that indicate a possibly higher  $T_g$  for Curithane LARC 160.

Rheological characterization was carried out on the 500g batches of AP-22 and Curithane 103 based LARC 160. The results were the same as those for the 200g batches; i.e., Curithane 103 based resin had a significantly lower minimum viscosity than the AP-22 based LARC. This, obviously, will result in higher flow and bleed-out during laminate processing. After reaching its minimum, the viscosity of the Curithane version then climbs quite rapidly, i.e. the slope and viscosity curve rise is greater than that of the AP-22 based version. The rheological curves are shown in Figures 4-11 and 4-12. Note that the curves for PMR-15 (Figure 4-13) and AP-22 based LARC 160 resemble each other far more than they resemble that of the Curithane 103 based LARC 160.

#### 5.0 LAMINATE PREPARATION

Since the bulk of the chemical and rheological characterization had centered on the AP-22 and Curithane 103 Version of LARC 160, it was determined that laminates should be fabricated from the two systems.

Standard commercial Fiberite prepreg was used in the AP-22 based laminate. Here LARC 160 is used to impregnate woven T-300 (8 harness satin) epoxy finish graphite cloth. The following cure schedule was used:

- (1) Heat at 2°C/minute to a temperature of 121°C.
- (2) Hold 90 min at 121°C, then heat at 2°C/min.
- (3) Pressurize to 1.2 MPa at 260°C.
- (4) Continue heating at 2°C/min to 330°C.
- (5) Hold 90 min at 330°C, 1.2 MPa, then cool under pressure to below 100°C.

A well consolidated laminate was made by this procedure.

From the rheological data generated on the LARC resin (Section 4) plus our experience in staging molding compounds (Section 3), it was apparent that the AP-22 cycle would need to be modified to successfully produce a Curithane based laminate. If the  $\eta^*$  curves are compared, the Curithane LARC 160 must be heated to 290°C to achieve a viscosity equivalent to that of the AP-22 LARC 160 at 260°C (pressurization point). It was, therefore, decided to use the AP-22 LARC 160 cure schedule listed above, but to pressurize at 290°C rather than 260°C.

A sample of the 500g batch of Curithane LARC 160 was applied to woven T-300 (8 HS), epoxy finish cloth reinforcement by a "dip and squee-gee" technique. The prepreg was air dried at ambient temperature overnight, followed by 4 hours at 93°C in a circulating air oven. The purpose of this bake was to eliminate solvent and thereby minimize plasticization and flow during cure. The resulting prepreg had a resin content of 46.8%. The laminate was laid up in a notched metal mold and press cured using the standard LARC 160 (AP-22) cycle, but applying pressure at 290°C. An apparently high quality laminate was successfully molded by this procedure.

Both the AP-22 and Curithane 103 based laminates were trimmed and sent to NASA/Langley.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 Conclusions

Several important results were obtained and conclusions reached during the course of the work:

- o PISO<sub>2</sub> could not be readily evaluated with our existing rheological techniques and equipment.
- o Imidized Curithane 103 based LARC 160 has significantly lower viscosity and therefore higher flow than AP-22 based LARC 160 during processing.
- o Rheological studies can be used to develop processing cycles for Curithane 103 based LARC 160 resin and prepreg.
- o Relatively small differences are found between the two uncured LARC 160 resins by conventional chemical characterization techniques.
- o Fully cured Curithane based LARC 160 may have a T<sub>g</sub> that is higher than that of AP-22 based LARC 160.

## 6.2 Recommendations

The following recommendations are made at this time:

- o Rheological techniques should be further explored and developed to characterize new resin and prepreg systems of interest and to define and develop efficacious processing schedules.
- o Although a pressurized rheological testing cell was not available in time for use on the program, one should be utilized to improve precision and accuracy when testing materials that evolve volatile species.
- o The characterization of Curithane 103 based LARC 160 should continue; it is quite different from AP-22 based LARC 160, both in processing and in the characteristics of the cured resin, and appears to have potential for use at temperatures approaching 400°C.

## 7.0 REFERENCES

- 1) Leaky, J. D., "Development and Demonstration of Manufacturing Processes for Fabricating Graphite/LARC 160 Polyimide Structural Elements", Contract NAS1-15371, 5th Quarterly Report, June through September, 1979.
- 2) Young, Philip R. and Sykes, George F., "Analysis of Aromatic Polyamine Mixtures for Formulation of LARC-160 Resin".
- 3) Leaky, J. D., "Development and Demonstration of Manufacturing processes for Fabricating Graphite/LARC 160 Polyimide Structural elements", Contract NAS1-15371, 9th Quarterly Report June through September, 1980.
- 4) Leaky, J. D., "Development and Demonstration of Manufacturing Process for Fabricating Graphite/LARC 160 Polyimide Structural Elements" Contract NAS1-15371, 2nd Quarterly Report September through December, 1978.



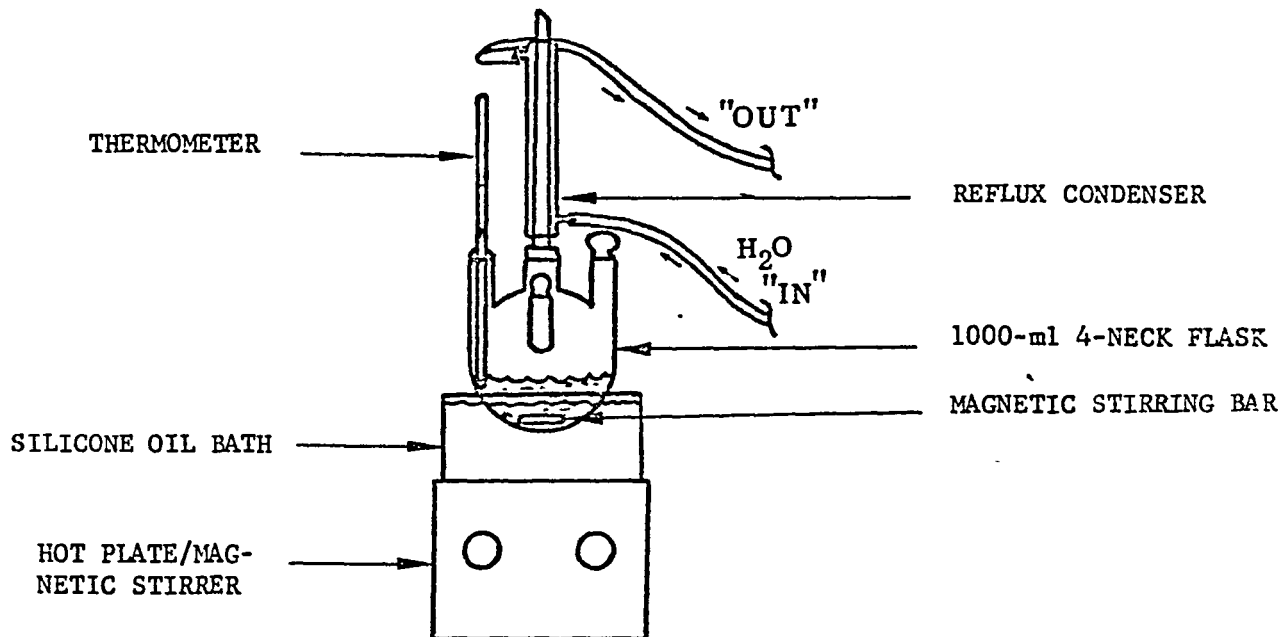
## APPENDIX

Contract No. NAS1-16287

### PROCEDURES RECOMMENDED BY FIBERITE CORP.

The synthesis of LARC 160 resin was performed as outlined below.

#### I. Set-Up



#### II. Reagents

BTDA (Eastman Lot #BOC)	35.617G	
NA (from Hexcel Corp.)	32.907G	
a. Ethanol (Sunny Sol, Tech. Grade)	50.0G	} Weighed into tared 100-ml graduate on top loading Mettler.
b. " " " " "	40.0G	
Jeffamine AP-22 (from Hexcel)	41.591G	- Weighed into a tared 100-ml beaker.

#### III. Procedure

1. The oil bath was preheated to about 70°C (158°F).
2. The ethanol contained rust from the 5 gallon can so was filtered through #42 Whatman paper before weighing it.
3. Added BTDA, NA and (a) EtOH into reaction (RXN) flask. Tried to mix with the stainless steel stirrer/air motor assembly but the blades were too small. Found a large magnetic stirring bar and tried that and it worked nicely.

## APPENDIX

### III. Continued

4. Lowered RXN vessel/condenser assembly into the heated oil and began heating mixture while continuously stirring.
5. The solid reagents went into solution at 66°C (151°F). Held at this reflux temperature for 1 hour. The hot plate had to be tweaked on and off to try and maintain a reasonably constant temperature. The fluctuation range was 66-72°C (151-162°F) but the majority of the time period the mixture refluxed between 66-69°C (151-156°F).
6. During the 1 hour refluxing, the beaker with the AP-22 was placed on an additional hot plate and heated to 79°C (175°F) to allow dissolution.
7. At the end of the 1 hour period the RXN vessel was removed from the oil bath, 1/2 ester sample removed and placed in a small vial, and the mixture allowed to cool to below 38°C (100°F).
8. The AP-22 and (b) EtOH were then added to the flask and mixed until homogeneous.
9. Since the resin was free of visual contaminants, it was poured directly into a glass jar and sealed.
10. Cleaned up glassware.

The synthesis of LARC 160 using Curithane 103 was performed. Clayton May called Terry St. Clair, NASA-Langley to confirm that the stoichiometry of AP-22 and Curithane 103 was the same - it is!

Using the set-up (I) and procedure (III) outlined above, the resin was made with the noted exceptions.

### II. Reagents

BTDA (Eastman, Lot #BOC)	35.612G	-	Weighed into tared 200-ml polypropylene beakers.
NA (from Hexcel)	32.915G	-	Weighed into tared 200-ml polypropylene beakers.
a. Ethanol (from Sunny Sol, Tech. Grade)	50.0G	}	Weighed into tared 100-ml graduate on Mettler top loader.
b. Ethanol " " " " "	40.1G		
Curithane 103 (from Hexcel)	41.513G	-	Weighed into tared 100-ml Pyrex beaker.

### Notes

1. Could not get Curithane out of can at room temperature to weigh it out. Preheated can in oven to 75° and then weighed it into tared beaker.
2. During refluxing, resin temperature got as high as 71°C (160°F) but on the average during the 1 hour period stayed within the range of 65-68°C (149-154°F).

## APPENDIX

### Notes (Cont.)

3. While lifting RXN vessel out to cool mix before adding curing agent, silicon oil was spilled all over hot plate; cleaned it up but very difficult to get off hands; contamination?
4. Curithane 103 does not melt as easily as Jeffamine AP-22. While preheating on the hot plate, material on the sides of the beaker remained crystalline as well as a crystalline "top" floating on the surface; should melt this material in an oven!!! Also should melt those in a closed container.
5. When pouring into the RXN vessel, the 103 resolidified quite rapidly; was able to dissolve most in EtOH (b) to transfer it from the beaker but still some crystalline blobs remained in resin and did not redissolve after considerable mixing.
6. Took entire resin solution up to 56°C while mixing to get a clear, homogeneous mix.
7. Poured resin into jar, sealed with polyethylene, capped, labelled, and submitted for viscosity measurements.
8. Cleaned up glassware.

Began the synthesis of PMR-15 as outlined below.

### I. Set-Up

Same as outlined above but used Sim-Ply-Trol pyrometer to monitor oil bath temperature; could not use to control hot plate since cycling also turned magnetic stirrer "off".

### II. Reagents

BTDA (Eastman, Lot #BOC)	43.001G	- Weighed into tared 200-ml polyethylene beakers.
NA (from Hexcel Corp.)	21.200G	- " " " " "
MDA	39.400G	- " " " " "
EtOH (Sunny Sol, Tech. Grade)	96.8G	- Weighed into tared 100-ml graduate on Mettler top loader.

### III. Procedure

1. Preheated oil bath to about 75°C (167°F).
2. Added BTDA, NA and EtOH into RXN flask.
3. Lowered RXN flask/condenser assembly into the oil bath and began stirring.
4. The resin temperature got up to 72.5°C (162°F) maximum; solids went into solution in about 15 minutes; by tweaking the hot plate during the first hour of refluxing, setting was found which held the resin temperature very constant at 67°C (152°F).

## APPENDIX

### III. Procedure (Cont.)

5. The mixture was refluxed for 7 hours at 67°C. Turned hot plate "off" and left stirrer and condenser H<sub>2</sub>O "on" all night.
6. Took 1/2 ester sample.
7. Added MDA flakes to RXN vessel.
8. Mixed for 1 hour at room temperature; most MDA flakes dissolved but a small amount of solid material still remained; continued mixing for 1 additional hour.
9. Let mixture stand about 1 hour then transferred it into a glass jar, sealed with a polyethylene liner, and submitted for viscosity measurements.

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15 Supplementary Notes Langley Technical Monitor: Dr. T. St. Clair Final Report					
16 Abstract  Chemical and rheological evaluation techniques were developed for polyimide composite matrix resins. LARC 160 (AP-22), LARC 160 (Curithane 103), PMR 15 and PISO <sub>2</sub> resins were investigated. Liquid and solid state rheological techniques were used to develop processing parameters and woven graphite reinforced laminates were successfully fabricated, using these processing parameters.					
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